same inventors

9/2003 09/632,011

EAST Browser - L14: (120) 13 and 1 | US 6465124 B1 | Tag: S | Doc: 10/120 (SORTED) | Format : KWIC

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	Document ID	Pages	1	3	U	S	C	P	Kind Codes	Sou
4	US 6528201 B1	21								USPAT
5	US 6517965 B1	10								USPAT
6	US 6498121 B1	13								USPAT
7	US 6497975 B2	8								USPAT
8	US 6471850 B2	9								USPAT
9	US 6468688 B2	139								USPAT
10	US 6465124 B1	5								USPAT

US-PAT-NO: 6465124

DOCUMENT-IDENTIFIER: US 6465124 B1

TITLE: Magnesium anode, seawater/acid/catholyte electrolyte utilizing a palladium and iridium carbon paper cathode electrochemical system

---------- KWIC ---------

TITLE - TI (1):
Magnesium anode, seawater/acid/catholyte electrolyte utilizing a palladium and iridium carbon paper cathode electrochemical system

Detailed Description Text - DETX (5):
The functioning magnesium-hydrogen peroxide semi-fuel cell of the present invention, as previously mentioned, is composed of a magnesium anode and an electrocatalyst of palladium and iridium catalyzed on carbon paper capable of reducing the hydrogen peroxide catholyte. Power is generated on the basis of an occurrence of the above reaction at the anode in which magnesium ions are formed and electrons released. The electrons are-transferred from the anode to the cathode by way of an external circuit in which the electrons perform work on a load. Electrolyte may be passed through the cell at any desired flow rate such as 200 cc/min and may be kept at an elevated temperature such as 55.degree. C. A useful electrolyte comprises 40 g/L seawater, 0.5 M hydrogen peroxide, and 0.1 M sulfuric acid in a two liter volume. A current density of 25 mA/cm.sup.2 may be applied to the electrode.

Detailed Description Text - DETX (7):
FIG. 1 graphically demonstrates the reason for achieving high voltages when palladium/iridium is catalyzed on a carbon paper substrate and tested under acid/seawater/catholyte electrolyte conditions wherein the electrolyte contains 0.1 M sulfuric acid and 0.5 M hydrogen peroxide and is at a temperature of 55.degree. C. The cell used in this test had a magnesium anode and an electrolyte flow rate of 200 cc/min. The silver foil demonstrates cathodic potentials of -0.4V vs silver/silver chloride (Ag/AgCl) at a current density of 25 mA/cm.sup.2 ; however, when the palladium/iridium on carbon paper is tested under the same conditions the cathodic voltage is increased to +0.4V vs Ag/AgCl. On a cell basis, an increase of 0.8V (800 mV) is expected due to the use of the palladium/iridium carbon electrode in the acid/seawater/catholyte electrolyte.

Detailed Description Text - DETX (8):
FIG. 2 shows a constant current discharge profile at 25 mA/cm.sup.2 when the aforementioned electrochemical system was tested. Observed were voltages above 2.12V when a carbon paper catalyzed with palladium/iridium was used in the seawater/acid electrolyte. Also pictured are the silver foil results showing cell voltages of 1.25V. A 70% increased in cell voltages was observed with the use of an acidic electrolyte and a palladium/iridium on carbon paper cathode.

Detailed Description Text - DETX (10):

(12) **United States Patent**
Medeiros et al.

(10) **Patent No.: US 6,465,124 B1**
(45) **Date of Patent: Oct. 15, 2002**

(54) **MAGNESIUM ANODE, SEAWATER/ACID/ CATHOLYTE ELECTROLYTE UTILIZING A PALLADIUM AND IRIDIUM CARBON PAPER CATHODE ELECTROCHEMICAL SYSTEM**

(75) Inventors: **Maria G. Medeiros, Bristol; Eric G. Dow, Barrington, both of RI (US); Russell R. Bessette, Mattapoisett, MA (US)**

(73) Assignee: **The United States of America as represented by the Secretary of the Navy, Washington, DC (US)**

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 68 days.

(21) Appl. No.: **09/632,012**
(22) Filed: **Jul. 28, 2000**
(51) **Int. Cl.**[7] **H01M 4/36**
(52) **U.S. Cl.** **429/105; 429/101**
(58) **Field of Search** 429/101, 105

(56) **References Cited**

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5,445,905 A * 8/1995 Marsh et al. 429/105

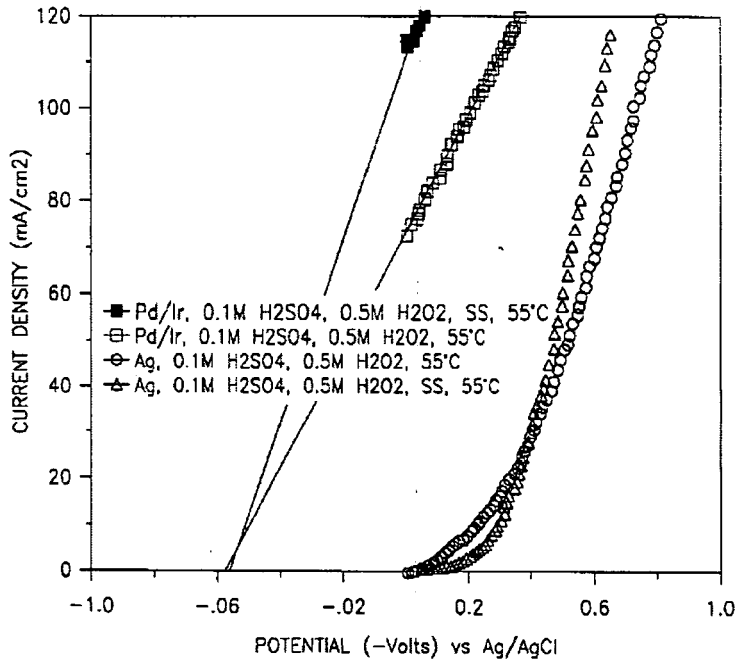
* cited by examiner

Primary Examiner—Carol Chaney
Assistant Examiner—Dah-Wei Yuan
(74) *Attorney, Agent, or Firm*—Michael J. McGowan; Prithvi C. Lall; Michael F. Oglo

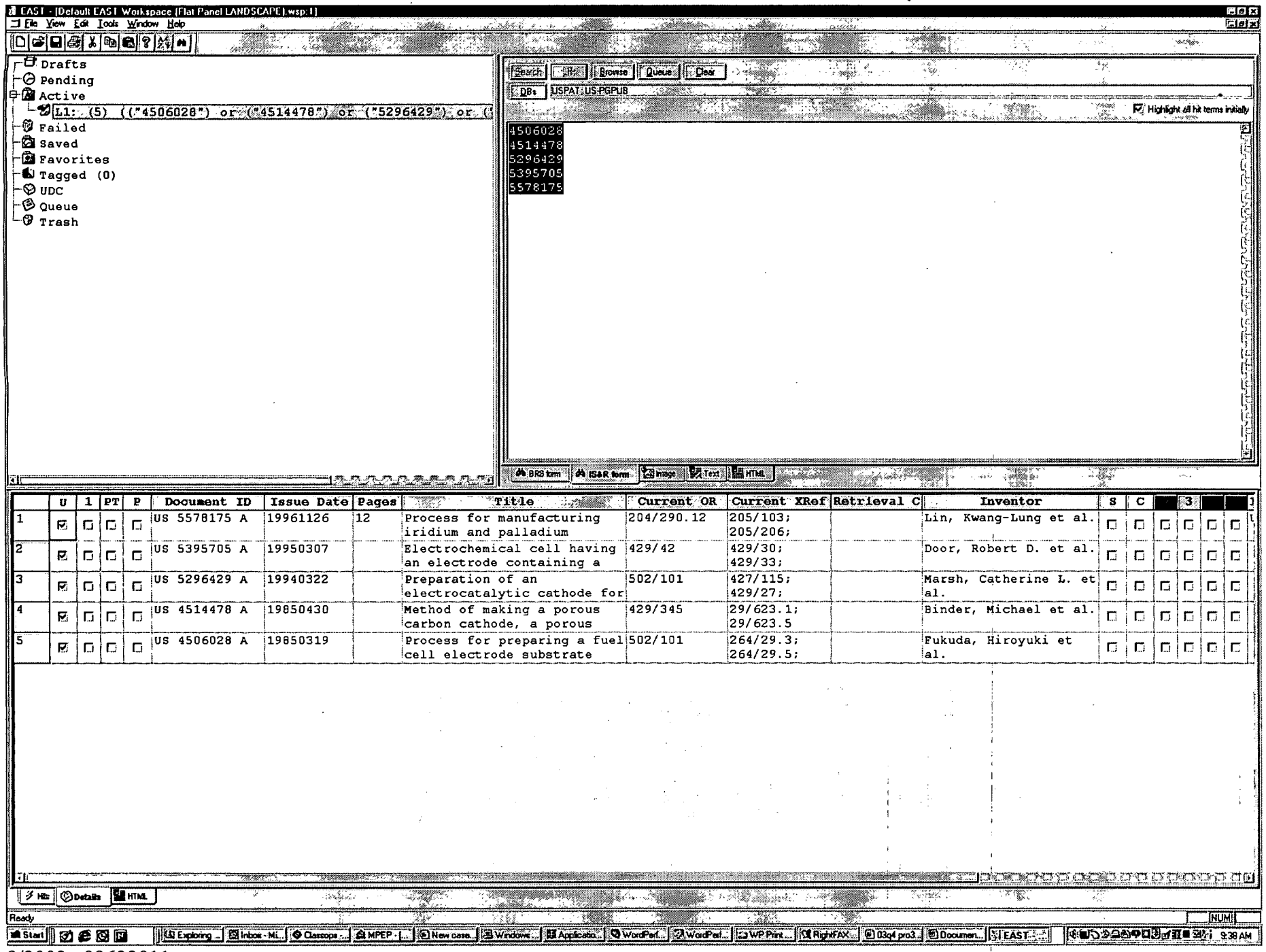
(57) **ABSTRACT**

The present invention relates to an improved magnesium semi-fuel cell which has a magnesium anode, a seawater/ catholyte electrolyte, preferably containing acid to solubilize solid precipitates, and an electrocatalyst composed of palladium and iridium catalyzed onto carbon paper. The acid added to the electrolyte is preferably selected from the group consisting of sulfuric acid, hydrochloric acid, phosphoric acid, acetic acid, and mixtures thereof.

7 Claims, 2 Drawing Sheets



prior art listed in spec



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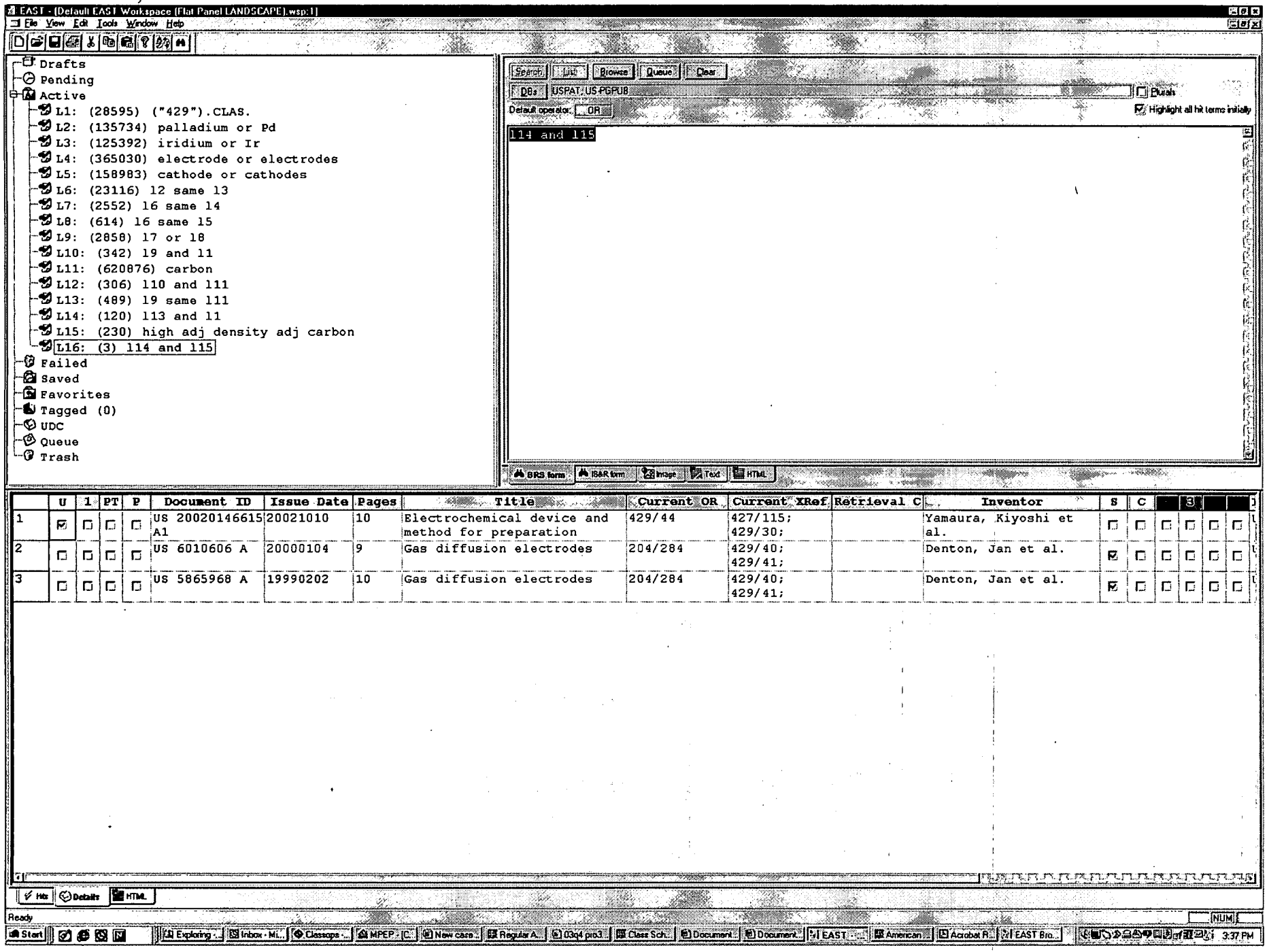
1	☑	☐	☐	☐	US 5578175 A	19961126	12	Process for manufacturing iridium and palladium	204/290.12	205/103; 205/206;		Lin, Kwang-Lung et al.	☐	☐	☐	☐	☐	☐
2	☑	☐	☐	☐	US 5395705 A	19950307		Electrochemical cell having an electrode containing a	429/42	429/30; 429/33;		Door, Robert D. et al.	☐	☐	☐	☐	☐	☐
3	☑	☐	☐	☐	US 5296429 A	19940322		Preparation of an electrocatalytic cathode for	502/101	427/115; 429/27;		Marsh, Catherine L. et al.	☐	☐	☐	☐	☐	☐
4	☑	☐	☐	☐	US 4514478 A	19850430		Method of making a porous carbon cathode, a porous	429/345	29/623.1; 29/623.5		Binder, Michael et al.	☐	☐	☐	☐	☐	☐
5	☑	☐	☐	☐	US 4506028 A	19850319		Process for preparing a fuel cell electrode substrate	502/101	264/29.3; 264/29.5;		Fukuda, Hiroyuki et al.	☐	☐	☐	☐	☐	☐



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1	☑	☐	☐	☐	US 20020146615 A1	20021010	10	Electrochemical device and method for preparation	429/44	427/115; 429/30;		Yamaura, Kiyoshi et al.	☐	☐
2	☐	☐	☐	☐	US 6010606 A	20000104	9	Gas diffusion electrodes	204/284	429/40; 429/41;		Denton, Jan et al.	☑	☐
3	☐	☐	☐	☐	US 5865968 A	19990202	10	Gas diffusion electrodes	204/284	429/40; 429/41;		Denton, Jan et al.	☑	☐

EAST Browser - L16: [3] 14 and 15 | US 5865968 A | Tag: S | Doc: 2/3 (SORTED) | Format : KWIC

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	Document ID	Pages	1		3			U	S	C	P	Kind Codes	Sourc
1	US 6010606 A	9											USPAT
2	US 5865968 A	10											USPAT
3	US 20020146615 A	10											US-PGPU

US-PAT-NO: 5865968

DOCUMENT-IDENTIFIER: US 5865968 A
See image for Certificate of Correction

TITLE: Gas diffusion electrodes

---------- KWIC ---------

Detailed Description Text - DETX (6):
A first embodiment of the present invention provides a gas diffusion electrode as hereinbefore described wherein the catalyst component is one or more metals or their oxides in the form of finely divided unsupported powders or as metals in a dispersed form on a carbon support. Suitably the one or more metals may be a precious metal (Pt, Pd, Ru, Rh, Ir, Os, Au and Ag) or a transition metal selected from groups IVB, VB, VIB, VIIB, VIII, IB or IIB of the Periodic Table in "Handbook of Chemistry and Physics", 64th Edition, CRC Press, or a combination or alloy thereof. Preferably, the one or more metals is a precious metal, particularly Pt, or an alloy thereof.

Detailed Description Text - DETX (27):
The electrode formed the cathode of an MEA, with the face of the electrode comprising the platinum catalyst component bonded to the membrane electrolyte face. The membrane employed was Du Pont NAFION 112. The single cell results are shown in FIG. 1 and demonstrate that good cell performances were obtained from the MEA comprising the lower cost, more manufacturable electrode of the invention. For operation on pure oxygen very high current densities of over 2.0 A/cm.sup.2 were obtained. For most practical applications of the PEMFC, the oxidant will be air, and these applications will require that at least a current density of 500 mA/cm.sup.2 is achieved. As illustrated in the Figure, current densities up to 1.0 A/cm.sup.2 were obtained, and the results represent performances typical of a satisfactorily performing MEA. It is worth noting that on air operation there was a tendency for the cell voltage to decrease more rapidly as the current density increased toward 1.0 A/cm.sup.2, compared to the pure oxygen data. This is an example of cell voltage decrease due to mass transport losses, relating to the ease with which reactant oxygen in air can diffuse to the electrode reaction sites. This is also a typical characteristic of cell current vs voltage plots seen with conventional MEAs, fabricated with electrodes comprising conducting substrates such as high density carbon fibre paper.

Current US Class - CLAS (2):
429

United States Patent [19]

Denton et al.

[11] **Patent Number: 5,865,968**

[45] **Date of Patent: Feb. 2, 1999**

[54] **GAS DIFFUSION ELECTRODES**

[75] Inventors: **Jan Denton**, Reading; **John M. Gascoyne**, High Wycombe; **Robert J. Potter**, Chalkhouse Green, all of United Kingdom

[73] Assignee: **Johnson Matthey Public Limited Company**, London, United Kingdom

[21] Appl. No.: **802,556**

[22] Filed: **Feb. 19, 1997**

[30] **Foreign Application Priority Data**

Feb. 28, 1996 [GB] United Kingdom 9604191
Dec. 23, 1996 [GB] United Kingdom 9626802

[51] **Int. Cl.**[6] **C25B 11/00**

[52] **U.S. Cl.** **204/284**; 429/40; 429/41; 429/42

[58] **Field of Search** 204/283, 284; 429/40, 41, 42

[56] **References Cited**

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4,680,100	7/1987	Morin	204/228
4,729,932	3/1988	McElroy	429/34
4,780,437	10/1988	Smith	502/101
4,894,355	1/1990	Takeuchi et al.	502/101
5,242,765	9/1993	Naimer et al.	428/42
5,292,600	3/1994	Kaufman	429/39
5,308,465	5/1994	Hillrichs et al.	204/283
5,322,744	6/1994	Koseki	429/13

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0226911	7/1987	European Pat. Off. .
0228602	7/1987	European Pat. Off. .
0499593	8/1992	European Pat. Off. .
582333	2/1994	European Pat. Off. .
654837	5/1995	European Pat. Off. .
62-156285	7/1987	Japan .
62-184768	8/1987	Japan .
62-232860	10/1987	Japan .
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1158580	7/1969	United Kingdom .
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"Management of the Water Content in Polymer Electrolyte Membranes with Porous Fiber Wicks" J. Electrochem. Soc., vol. 140, No. 11, pp. 3190–3193, Nov. 1993.

Primary Examiner—Bruce F. Bell
Attorney, Agent, or Firm—Stevens, Davis, Miller & Mosher, L.L.P.

[57] **ABSTRACT**

A gas diffusion electrode comprising a non-woven network of fibres, one or more catalysts components and at least one polymeric substance characterized in that the catalyst is embedded within the fibre network is disclosed.

20 Claims, 2 Drawing Sheets

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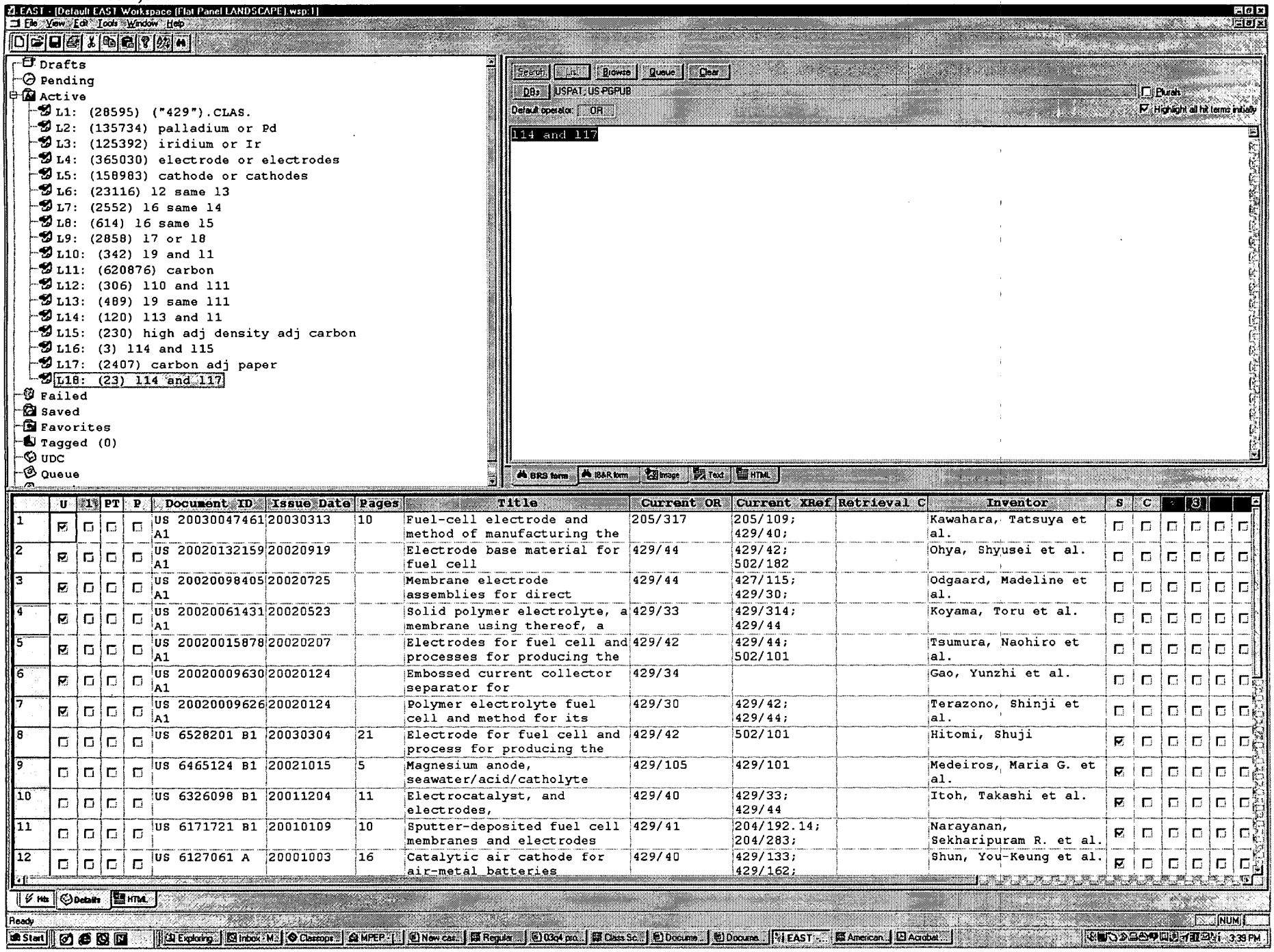

	U	1	PT	P	Document ID	Issue Date	Pages	Title	Current OR	Current XRef	Retrieval C	Inventor	S	C		3		
1	☑	☐	☐	☐	US 20030047461 A1	20030313	10	Fuel-cell electrode and method of manufacturing the	205/317	205/109; 429/40;		Kawahara, Tatsuya et al.	☐	☐	☐	☐	☐	☐
2	☑	☐	☐	☐	US 20020132159 A1	20020919		Electrode base material for fuel cell	429/44	429/42; 502/182		Ohya, Shyusei et al.	☐	☐	☐	☐	☐	☐
3	☑	☐	☐	☐	US 20020098405 A1	20020725		Membrane electrode assemblies for direct	429/44	427/115; 429/30;		Odgaard, Madeline et al.	☐	☐	☐	☐	☐	☐
4	☑	☐	☐	☐	US 20020061431 A1	20020523		Solid polymer electrolyte, a membrane using thereof, a	429/33	429/314; 429/44		Koyama, Toru et al.	☐	☐	☐	☐	☐	☐
5	☑	☐	☐	☐	US 20020015878 A1	20020207		Electrodes for fuel cell and processes for producing the	429/42	429/44; 502/101		Tsumura, Naohiro et al.	☐	☐	☐	☐	☐	☐
6	☑	☐	☐	☐	US 20020009630 A1	20020124		Embossed current collector separator for	429/34			Gao, Yunzhi et al.	☐	☐	☐	☐	☐	☐
7	☑	☐	☐	☐	US 20020009626 A1	20020124		Polymer electrolyte fuel cell and method for its	429/30	429/42; 429/44;		Terazono, Shinji et al.	☐	☐	☐	☐	☐	☐
8	☐	☐	☐	☐	US 6528201 B1	20030304	21	Electrode for fuel cell and process for producing the	429/42	502/101		Hitomi, Shuji	☑	☐	☐	☐	☐	☐
9	☐	☐	☐	☐	US 6465124 B1	20021015	5	Magnesium anode, seawater/acid/catholyte	429/105	429/101		Medeiros, Maria G. et al.	☑	☐	☐	☐	☐	☐
10	☐	☐	☐	☐	US 6326098 B1	20011204	11	Electrocatalyst, and electrodes,	429/40	429/33; 429/44		Itoh, Takashi et al.	☑	☐	☐	☐	☐	☐
11	☐	☐	☐	☐	US 6171721 B1	20010109	10	Sputter-deposited fuel cell membranes and electrodes	429/41	204/192.14; 204/283;		Narayanan, Sekharipuram R. et al.	☑	☐	☐	☐	☐	☐
12	☐	☐	☐	☐	US 6127061 A	20001003	16	Catalytic air cathode for air-metal batteries	429/40	429/133; 429/162;		Shun, You-Keung et al.	☑	☐	☐	☐	☐	☐

EAST Browser - L10: [23] 14 and 17 | US 6010606 A | Tag: S | Doc: 6/23 [SORTED] | Format : KWIC

File Edit View Tools Window Help

	Document ID	Pages	1	2	3	U	S	C	P	Kind Codes	Sou
1	US 6528201 B1	21									USPAT
2	US 6465124 B1	5									USPAT
3	US 6326098 B1	11									USPAT
4	US 6171721 B1	10									USPAT
5	US 6127061 A	16									USPAT
6	US 6010606 A	9									USPAT
7	US 5865968 A	10									USPAT

US-PAT-NO: 6010606

DOCUMENT-IDENTIFIER: US 6010606 A

TITLE: Gas diffusion electrodes

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Brief Summary Text - BSTX (9):
These catalyst layers are usually formed into suitable mixtures of the components and deposited onto a suitable porous substrate, for example conducting carbon materials such as semi graphitised papers, cloths or foams, or particularly in the case of alkaline electrolyte systems, metal meshes such as nickel or stainless steel, or in the case of sensors, various forms of porous PTFE sheet. In the acid electrolyte PEMFC the substrate is usually based on carbon paper or woven cloth materials (EP 0 026 995). These materials generally have a high bulk fibre density of greater than 0.4 g/cm.sup.3. The primary role of the substrate is to act as a physical support for the catalyst containing layers and to provide an electrically conducting structure in direct contact with the catalyst layer. Additionally it also enables a mechanically stable gas diffusion electrode to be produced.

Detailed Description Text - DETX (6):
A first embodiment of the present invention provides a gas diffusion electrode as hereinbefore described wherein the catalyst component is one or more metals or their oxides in the form of finely divided unsupported powders or as metals in a dispersed form on a carbon support. Suitably the one or more metals may be a precious metal (Pt, Pd, Ru, Rh, Ir, Os, Au and Ag) or a transition metal selected from groups IVB, VB, VIB, VIIB, VIII, IB or IIB of the Periodic Table in "Handbook of Chemistry and Physics", 64th Edition, CRC Press, or a combination or alloy thereof. Preferably, the one or more metals is a precious metal, particularly Pt, or an alloy thereof.

Detailed Description Text - DETX (8):
A major advantage of the present invention is that a free-standing, dimensionally stable and highly flexible gas diffusion electrode is obtained. The incidence of damage to the electrode on handling during manufacture is therefore minimised thus reducing the number of faulty or rejected electrodes, and consequently the cost is reduced. Furthermore, the intrinsic material cost is significantly reduced over carbon paper or woven cloths. In addition, the electrode of the invention is more amenable to high volume continuous production processes due to its high dimensional stability.

Current US Class - CLAS (2):
429

United States Patent [19]

Denton et al.

[11] **Patent Number: 6,010,606**

[45] **Date of Patent: Jan. 4, 2000**

[54] **GAS DIFFUSION ELECTRODES**

[75] Inventors: **Jan Denton**, Reading; **John M Gascoyne**, High Wycombe; **Robert J Potter**, South Oxon, all of United Kingdom

[73] Assignee: **Johnson Matthey Public Limited Company**, London, United Kingdom

[21] Appl. No.: 09/189,842

[22] Filed: Nov. 12, 1998

Related U.S. Application Data

[62] Division of application No. 08/802,556, Feb. 19, 1997, Pat. No. 5,865,968.

[30] **Foreign Application Priority Data**

Feb. 28, 1996 [GB] United Kingdom 9604191
Dec. 23, 1996 [GB] United Kingdom 9626802

[51] **Int. Cl.**[7] **C25B 11/00**

[52] **U.S. Cl.** **204/284**; 429/40; 429/41; 429/42

[58] **Field of Search** 204/283, 284; 429/40, 41, 42; 427/115

[56] **References Cited**

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3,972,735	8/1976	Breault	136/122
4,115,627	9/1978	Christner et al.	429/44
4,185,131	1/1980	Goller et al.	427/115
4,680,100	7/1987	Morin	204/228
4,729,932	3/1988	McElroy	429/34
4,780,437	10/1988	Smith	502/101
4,894,355	1/1990	Takeuchi et al.	502/101
5,242,765	9/1993	Naimer et al.	429/42
5,292,600	3/1994	Kaufman	429/39
5,308,465	5/1994	Hillriche et al.	204/283
5,322,744	6/1994	Koseki	429/13

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0226280	6/1987	European Pat. Off. .
0226911	7/1987	European Pat. Off. .
0228602	7/1987	European Pat. Off. .
0499593	8/1992	European Pat. Off. .
582333	2/1994	European Pat. Off. .
654837	5/1995	European Pat. Off. .
62-156285	7/1987	Japan .
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62-232860	10/1987	Japan .
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6267555	9/1994	Japan .
0981918	1/1965	United Kingdom .
1158580	7/1969	United Kingdom .
1467147	3/1977	United Kingdom .

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"Management of the Water Content in Polymer Electrolyte Membranes with Porous Fiber Wicks" J. Electrochem, Soc., vol. 140, No. 11, pp. 3190–3193, Nov. 1993.

Primary Examiner—Bruce F. Bell
Attorney, Agent, or Firm—Stevens, Davis, Miller & Mosher, L.L.P.

[57] **ABSTRACT**

A gas diffusion electrode comprising a non-woven network of fibers, one or more catalysts components and at least one polymeric substance characterised in that the catalyst is embedded within the fiber network is disclosed.

49 Claims, 2 Drawing Sheets

EAST Browser - L18: [23] 14 and 17 | US 5350643 A | Tag: S | Doc: 12/23 (SORTED) | Format : KWIC

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7	US 5865968 A	10			☑				USPAT
8	US 5783325 A	14			☑				USPAT
9	US 5716437 A	13			☑				USPAT
10	US 5635039 A	26			☑				USPAT
11	US 5521020 A	10			☑				USPAT
12	US 5350643 A	9			☑				USPAT
13	US 5217821 A	8			☑				USPAT

US-PAT-NO: 5350643

DOCUMENT-IDENTIFIER: US 5350643 A

TITLE: Solid polymer electrolyte type fuel cell

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Detailed Description Text - DETX (5):
According to the present invention, the catalyst layers in both the hydrogen electrode and the oxygen electrode comprise a carbon carrier, an active component (catalyst) supported thereon, a proton conductor and a water repellent binder. The active component is preferably platinum or platinum group metals such as rhodium, ruthenium, palladium and iridium and materials of the proton conductor may be the same as or different from the solid polymer electrolyte. Furthermore, the water repellent binder is preferably a fluorocarbon polymer such as polytetrafluoroethylene (PTFE) or graphite fluoride represented by the formula (CF).sub.n or a mixture thereof.

Detailed Description Text - DETX (19):
An electrode catalyst comprising carbon powders on which platinum was supported was sufficiently kneaded with a perfluorosulfonic acid ion-exchange resin (Nafion liquid manufactured by Aldrich Chemical Co.) as a proton conductor and an aqueous suspension of PTFE to prepare a paste. This paste was coated on a carbon paper of about 100 .mu.m in pore diameter and 100 .mu.m thick coated with PTFE which was an electron conductor (gas diffusion layer). This was dried at 80.degree. C. to obtain an electrode. The above electron conductor was obtained by coating an aqueous suspension of PTFE on the carbon paper at a coating amount of 12 mg/cm.sup.2 and firing it at 350.degree. C. The composition of the hydrogen electrode was as follows: amount of platinum: 0.3 mg/cm.sup.2, amount of the above proton conductor: 30% by weight and amount of PTFE: 30% by weight. The composition of the oxygen electrode was as follows: amount of platinum: 0.3 mg/cm.sup.2 amount of the above proton conductor: 20% by weight and amount of PTFE: 20% by weight.

Detailed Description Text - DETX (23):
Electrodes were prepared in the following manner. A catalyst comprising a carbon carrier on which platinum was supported and a perfluorocarboxylic acid resin which was a proton conductor were sufficiently kneaded to obtain a catalyst paste. This paste was rolled by a roll press to obtain a plurality of sheets. These sheets were impregnated with an aqueous PTFE suspension having a PTFE concentration of 20% by weight and dried at 80.degree. C. to obtain sheet-like catalyst layers. Then, these sheet-like catalyst layers were impregnated with another aqueous PTFE suspension having a PTFE concentration different from that of the above suspension and dried at 80.degree. C. In this way, electrodes were prepared in which the catalyst layer of both the hydrogen electrode and the oxygen electrode had a concentration gradient of the water-repellant in the thickness direction of the catalyst layer. The catalyst layer of the hydrogen electrode had such a concentration gradient of the water-repellant as 20% by weight in the portion facing to the electrolyte membrane and 40% by weight in the portion facing to the gas diffusion layer. The catalyst layer of the oxygen electrode had such a concentration gradient of the water-repellant as 10% by weight in the portion facing to the electrolyte

United States Patent [19]

Imahashi et al.

[11] **Patent Number: 5,350,643**

[45] **Date of Patent: Sep. 27, 1994**

[54] **SOLID POLYMER ELECTROLYTE TYPE FUEL CELL**

[75] Inventors: Jinichi Imahashi; Tatsuo Horiba, both of Hitachi; Yasushi Muranaka, Katsuta, all of Japan

[73] Assignee: Hitachi, Ltd., Tokyo, Japan

[21] Appl. No.: 69,579

[22] Filed: Jun. 1, 1993

[30] Foreign Application Priority Data

Jun. 2, 1992 [JP] Japan 4-165459

[51] Int. Cl.[5] H01M 8/10; H01M 4/86

[52] U.S. Cl. 429/33; 429/30; 429/41; 429/42

[58] Field of Search 429/30, 42, 41, 33

[56] References Cited

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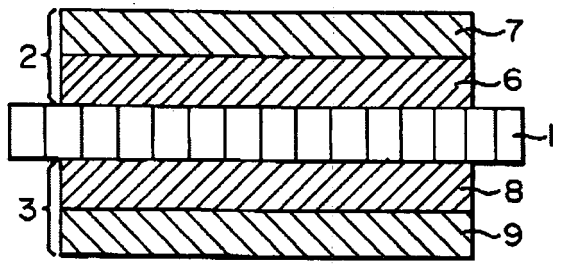
Primary Examiner—John S. Maples

Attorney, Agent, or Firm—Antonelli, Terry, Stout & Kraus

[57] **ABSTRACT**

Provided is a solid polymer electrolyte type fuel cell which is improved in cell output characteristics by preventing the flooding phenomenon at the interface between the oxygen electrode and the electrolyte membrane, accelerating the gas diffusion and effective utilization of the active surface of the catalyst. This solid polymer electrolyte type fuel cell comprises solid polymer electrolyte membrane 1 and gas diffusion electrodes 2 and 3 provided on both sides of the membrane, said gas diffusion electrodes comprising catalyst layers 6 and 8 and gas diffusion layers 7 and 9 being provided on the outer side of the respective catalyst layers and a hydrogen-containing gas and an oxygen-containing gas being fed to the respective electrodes. In this cell, the water-repellency of the hydrogen electrode 2 is higher than that of the oxygen electrode 3 and furthermore, a gradient of water-repellency is provided in the catalyst layer of each electrode so that the water-repellency in the portion facing to the electrolyte membrane is higher than that in the portion facing to the gas diffusion layer in each catalyst layer. The output density of the cell according to the present invention is as high as 2-3 times that of conventional cells.

11 Claims, 3 Drawing Sheets



EAST Browser - L18: [23] 14 and 17 | US 3899354 A | Tag: S | Doc: 16/23 (SORTED) | Format : KWIC

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12	US 5350643 A	9							☑					USPAT
13	US 5217821 A	8							☑					USPAT
14	US 4293396 A	8							☑					USPAT
15	US 4248682 A	9							☑					USPAT
16	US 3899354 A	8							☑					USPAT
17	US 20030047461 A	10							☑					US-PG

US-PAT-NO: 3899354

DOCUMENT-IDENTIFIER: US 3899354 A
See image for Certificate of Correction

TITLE: Gas electrodes and a process for producing them

---------- KWIC ---------

Brief Summary Text - BSTX (22):
As used herein, carbon paper shall mean a sheet of fibrous carbon made by a paper making process.

Brief Summary Text - BSTX (23):
As used herein, a thin porous conductive substrate shall mean a thin fibrous or porous sheet between about 3 mils (0.00762 cm) and about 15 mils (0.0381 cm) thick, preferably about 10 mils (0.0254 cm) thick, such as carbon paper, carbon cloth, carbon felt, carbon tape, and the like. Also, any porous metal screen, expanded metal, metal felt or mesh which is electrically conductive and able to withstand the corrosive environment of a fuel cell can be used. Examples of metal sheets suitable for use in this invention include nickel, iron, titanium, tantalum, zirconium, gold, silver and alloys thereof, depending on the choice of electrolyte.

Detailed Description Text - DETX (2):
A number of platinized gas electrodes were fabricated in the following manner. Carbon paper, Grade VDL as supplied by Union Carbide Corporation, measuring 6 inches (15.24 cm) by 6 inches (15.24 cm) by 14 mils (0.0356 cm) thick, was sprayed with an aqueous polytetrafluoroethylene suspension containing 55 weight percent polytetrafluoroethylene, until the carbon paper was saturated. Thereafter the carbon paper was cured by heating to 325.degree.C. in a nitrogen atmosphere for 30 minutes.

Claims Text - CLTX (2):
2. The gas electrode of claim 1 wherein said substrate comprises a material selected from the group consisting of carbon paper, carbon cloth, carbon tape, carbon felt, metal screen, expanded metal, metal mesh and metal felt; wherein said porous conductive first layer comprises activated carbon and a material selected from the group consisting of polytetrafluoroethylene, polyethylene, polytrifluorochloroethylene, polyvinylfluoride, polyvinylchloride, polyvinylidenefluoride, polyvinylidenechloride neoprene, styrene-butadiene copolymer and natural waxes; and wherein said noble metal is selected from the group consisting of platinum, rhodium, ruthenium, palladium, osmium, iridium, silver, gold and mixtures and alloys thereof.

Claims Text - CLTX (7):
7. The gas electrode of claim 1 for use with immobilized phosphoric acid fuel cells wherein said porous wetproofed conductive substrate is carbon paper coated with polytetrafluoroethylene; said water-repellent porous active conductive layer is activated carbon and polytetrafluoroethylene; and said noble metal is platinum.

United States Patent [19]

Kordesch

[11] **3,899,354**

[45] **Aug. 12, 197**

[54] **GAS ELECTRODES AND A PROCESS FOR PRODUCING THEM**

[75] Inventor: **Karl V. Kordesch, Lakewood, Ohio**

[73] Assignee: **Union Carbide Corporation, New York, N.Y.**

[22] Filed: **Sept. 10, 1973**

[21] Appl. No.: **395,552**

[52] U.S. Cl. ..... 136/86 D; 136/120 FC
[51] Int. Cl. H01m 27/04
[58] Field of Search ..... 136/86 D, 86 R, 120 FC, 136/120, 122

[56] References Cited

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Primary Examiner—John H. Mack
Assistant Examiner—H. A. Feeley
Attorney, Agent, or Firm—C. F. O'Brien

[57] **ABSTRACT**

A thin catalyzed gas electrode for fuel cells comprising a porous wet proofed conductive substrate having a first water-repellent porous active conductive layer over which is a surface-deposited noble metal catalyst in an amount of at least about 0.5 mg/cm², and a process for producing such an electrode.

12 Claims, No Drawings

EAST Browser - L3: [20] 1 and 2 | US 6290839 B1 | Tag: S | Doc: 3/20 (SORTED)

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2	US 6303016 B1	14								USPAT
3	US 6290839 B1	66								USPAT
4	US 6264825 B1	75								USPAT
5	US 6248229 B1	25								USPAT
6	US 6110354 A	31								USPAT
7	US 6013459 A	18								USPAT

US-PAT-NO: 6290839

DOCUMENT-IDENTIFIER: US 6290839 B1

TITLE: Systems for electrophoretic transport and detection of analytes

---------- KWIC ---------

Detailed Description Text - DETX (342):
In a preferred embodiment, electronic detection is used, including amperommetry, voltammetry, capacitance, and impedence. Suitable techniques include, but are not limited to, electrogravimetry; coulometry (including controlled potential coulometry and constant current coulometry); voltametry (cyclic voltametry, pulse voltametry (normal pulse voltametry, square wave voltametry, differential pulse voltametry, Osteryoung square wave voltametry, and coulostatic pulse techniques); stripping analysis (aniodic stripping analysis, cathiodic stripping analysis, square wave stripping voltammetry); conductance measurements (electrolytic conductance, direct analysis); time-dependent electrochemical analyses (chronoamperometry, chronopotentiometry, cyclic chronopotentiometry and amperometry, AC polography, chronogalvametry, and chronocoulometry); AC impedance measurement; capacitance measurement; AC voltametry; and photoelectrochemistry.

Current US Class - CLAS (2):
205

(12) **United States Patent**
Kayyem et al.

(10) **Patent No.: US 6,290,839 B1**
(45) **Date of Patent: *Sep. 18, 2001**

(54) **SYSTEMS FOR ELECTROPHORETIC TRANSPORT AND DETECTION OF ANALYTES**

(75) Inventors: **Jon Faiz Kayyem**, Pasadena; **Gary Blackburn**, Glendora; **Stephen D. O'Connor**, Pasadena, all of CA (US)

(73) Assignee: **Clinical Micro Sensors, Inc.**, Pasadena, CA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

This patent is subject to a terminal disclaimer.

(21) Appl. No.: **09/134,058**

(22) Filed: **Aug. 14, 1998**

Related U.S. Application Data

(60) Provisional application No. 60/090,389, filed on Jun. 23, 1998.

(51) **Int. Cl.**[7] **G01N 27/26**

(52) **U.S. Cl.** **205/777.5**; 204/403; 204/450; 204/452; 204/409; 204/600; 204/603

(58) **Field of Search** 204/403, 415, 204/409, 451, 456, 601, 606, 452, 602, 450, 600; 422/68.1; 435/6, 183; 205/777.5, 775

(56) **References Cited**

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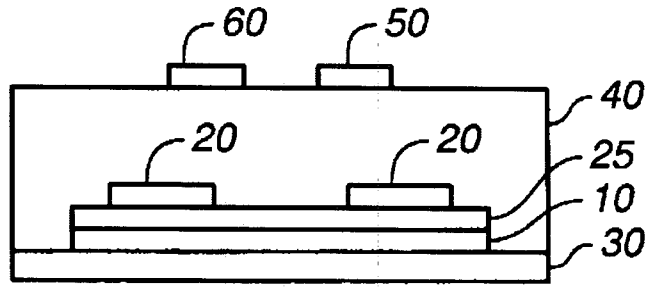
Primary Examiner—T. Tung
Assistant Examiner—Alex Noguerola
(74) *Attorney, Agent, or Firm*—Fehr Hohbach Test Albritton & Herbert LLP; Richard F. Trecartin, Esq.; Robin M. Silva, Esq.

(57) **ABSTRACT**

The invention relates to compositions and methods useful in the electrophoretic transport of target analytes to a detection electrode comprising a self-assembled monolayer (SAM). Detection proceeds through the use of an electron transfer moiety (ETM) that is associated with the target analyte, either directly or indirectly, to allow electronic detection of the ETM.

28 Claims, 21 Drawing Sheets



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8	US 6013170 A	19											USPAT
9	US 5645709 A	21											USPAT
10	US 5382331 A	16											USPAT
11	US 5059290 A	8											USPAT

US-PAT-NO: 5059290

DOCUMENT-IDENTIFIER: US 5059290 A

TITLE: Electroanalytical method

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Detailed Description Text - DETX (26):
Using as a working electrolyte, an aqueous solution of acetic acid-sodium acetate containing KI of pH 3.5 and on the other hand, using as a counter electrode solution, an aqueous solution of acetic acid-sodium acetate containing iodine and iodine ion and at a potential of the working electrode of -0.5V vs. the counter electrode, residual chlorine in tap water was determined (controlled potential coulometry).

Detailed Description Text - DETX (51):
The determination in Example 4 was carried out according to a constant-current method of seeking the endpoint from change in the potential. As a result, the determination could be carried out with an accuracy almost same with that in the case of controlled potential coulometry.

Detailed Description Text - DETX (62):
The concentration of L-ascorbic acid of reduced type in various foods were measured according to controlled potential coulometry using ferricyan ion as oxidation mediator. The construction of the detector was made as follows:

Current US Class - CLAS (2):
205

United States Patent [19]

Uchiyama et al.

[11] **Patent Number: 5,059,290**

[45] **Date of Patent: Oct. 22, 1991**

[54] **ELECTROANALYTICAL METHOD**

[75] Inventors: Shunichi Uchiyama, Fukaya; Shuichi Suzuki, Tokyo, both of Japan

[73] Assignee: Mitsui Engineering & Shipbuilding Co., Ltd., Tokyo, Japan

[21] Appl. No.: 301,792

[22] Filed: Jan. 25, 1989

[30] Foreign Application Priority Data

Jan. 29, 1988 [JP] Japan 63-18696

[51] Int. Cl.[5] G01N 27/26

[52] U.S. Cl. 204/153.1; 204/153.12; 204/400; 204/403; 204/409

[58] Field of Search ..... 204/1 T, 400, 409, 435, 204/431, 432, 403, 153.1, 153.12

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87/03624 6/1987 PCT Int'l Appl. .

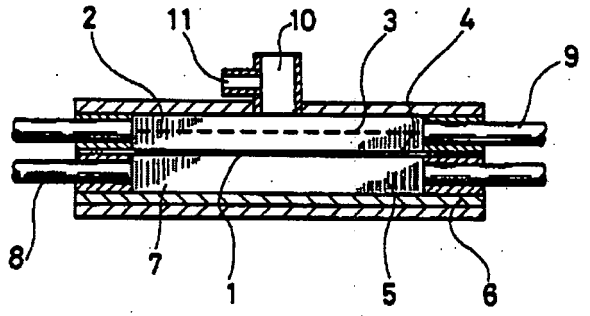
Primary Examiner—T. Tung

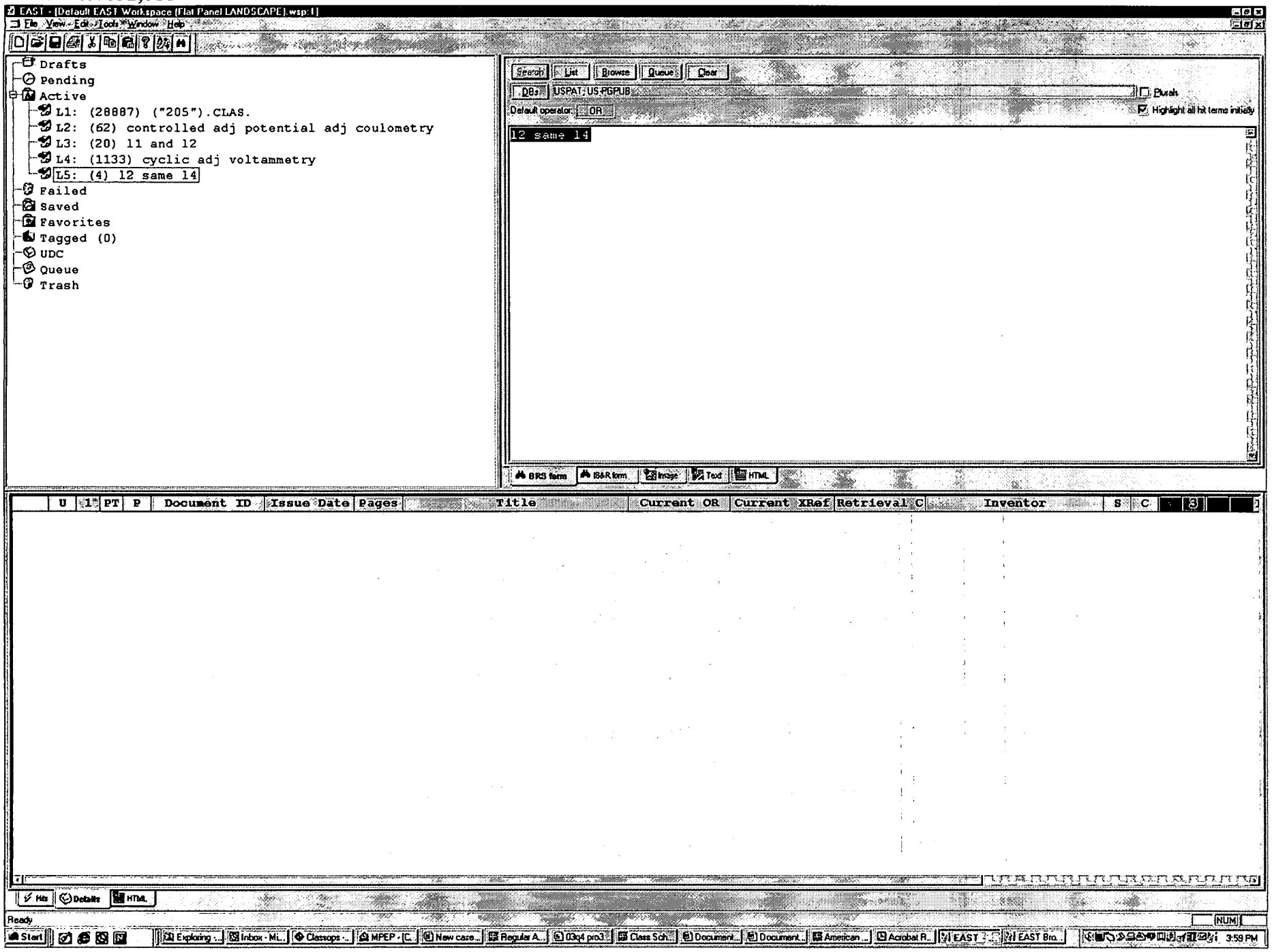
Attorney, Agent, or Firm—Fay, Sharpe, Beall, Fagan, Minnich & McKee

[57] ABSTRACT

An electroanalytical method which can detect and determine a substance in a short time, with stability and simply is provided, which method comprises providing an electrolytic cell provided with a working electrode chamber and a counter electrode chamber adjacent thereto by the medium of a separator electrolyzing a sample to be determined, by feeding it to a working electrode contained in the working electrode chamber and consisting of an electroconductive porous body impregnated with an electrolyte in a non-flowing state; and measuring at least one of the electric voltage, electric current and electrical quantity in the working electrode, to determine the substance in the sample.

8 Claims, 2 Drawing Sheets

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3	US 4410402 A	8							☑				USPAT
4	US 20020177135 A	93							☑				US-PGPU

US-PAT-NO: 6110354

DOCUMENT-IDENTIFIER: US 6110354 A
See image for Certificate of Correction

TITLE: Microband electrode arrays

---------- KWIC ---------

Detailed Description Text - DETX (39):
The type of analyte to be detected and/or identified will affect the choice of electrochemical technique to be employed. For instance, anodic stripping voltammetry is employed when the redox-active analyte is a metal, while cathodic stripping voltammetry is used for detection of anions, such as chloride and bromide. These techniques include, but are not limited to, electrogravimetry; controlled-potential coulometry; controlled-current coulometry; voltammetry; anodic- and cathodic-stripping voltammetry; cyclic voltammetry; square wave voltammetry; differential pulse voltammetry; adsorptive stripping voltammetry; potentiometric stripping analysis and amperometry. U.S. patent application Ser. No. 08/738,445 filed Oct. 25, 1996; Gary D. Christian, Analytical Chemistry, 4th ed., John Wiley and Sons, Inc. (1986)); A. Bard and L. R. Faulkner, Electrochemical Methods: Fundamentals and Applications, John Wiley, (1980); and P. t. Kissinger and W. Heineman, Eds., Laboratory Techniques in Electroanalytical Chemistry, 2nd ed., Marcell Dekker, (1990) describe many electrochemical techniques, and all of these references are incorporated in their entirety by reference herein.

United States Patent [19]

Saban et al.

[11] **Patent Number: 6,110,354**

[45] **Date of Patent: Aug. 29, 2000**

[54] **MICROBAND ELECTRODE ARRAYS**

[75] Inventors: **Steven Saban**, Snohomish; **Robert B. Darling**, Lake Forest Park; **Paul Yager**, Seattle, all of Wash.

[73] Assignee: **University of Washington**, Seattle, Wash.

[21] Appl. No.: **08/963,678**

[22] Filed: **Oct. 31, 1997**

Related U.S. Application Data

[60] Provisional application No. 60/030,319, Nov. 1, 1996.

[51] **Int. Cl.**[7] **G01N 27/26**

[52] **U.S. Cl.** **205/775**; 204/412; 204/413; 204/434

[58] **Field of Search** 204/412, 413, 204/434; 205/775

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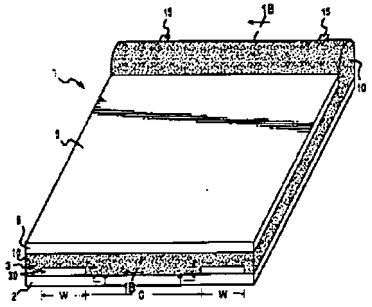
(List continued on next page.)

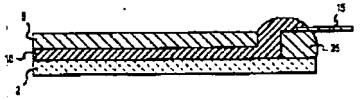
Primary Examiner—Robert J. Warden, Sr.
Assistant Examiner—Jennifer McNeil
Attorney, Agent, or Firm—Greenlee, Winner & Sullivan, P.C.

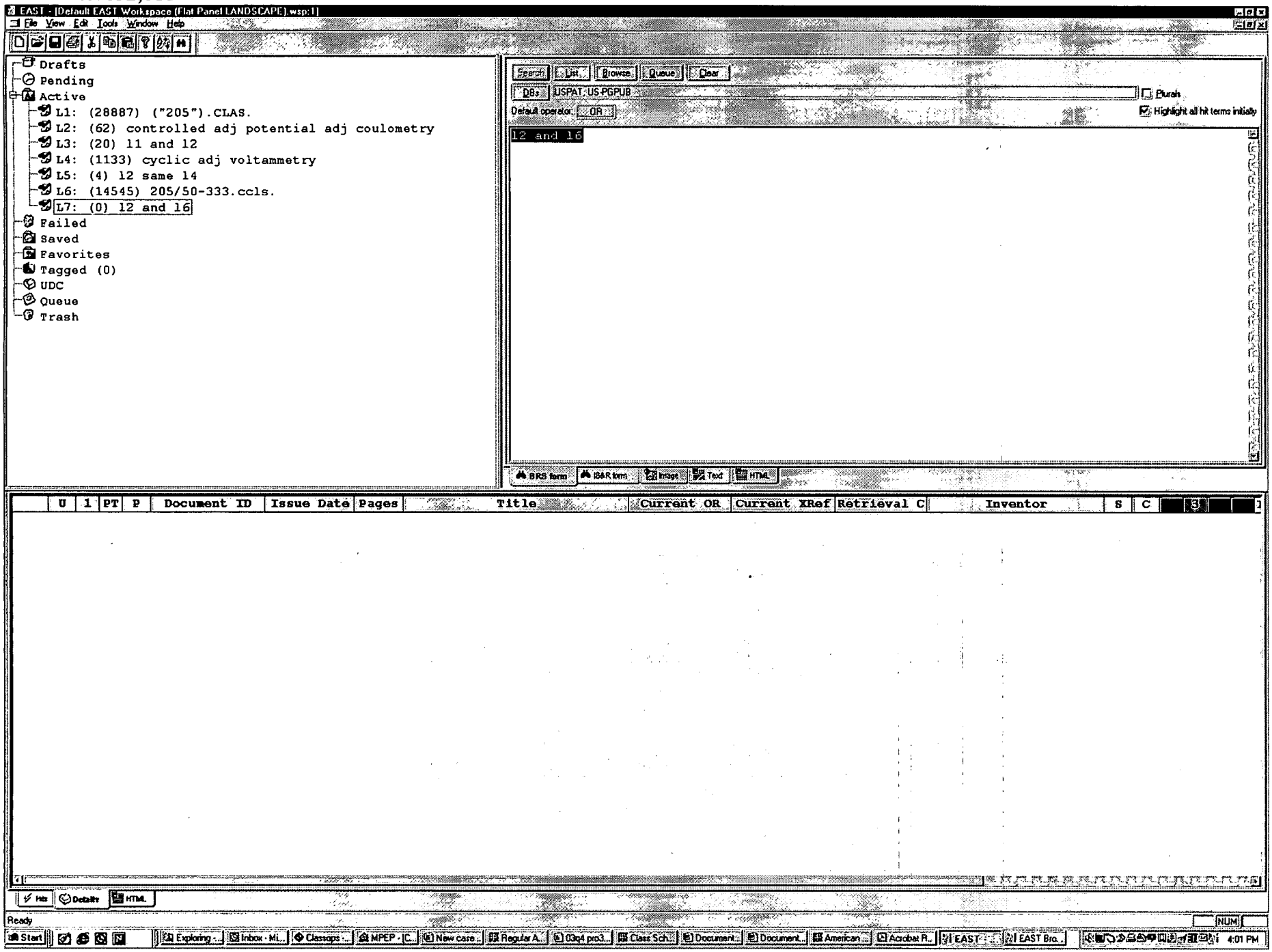
[57] **ABSTRACT**

The present invention provides microband electrode array sensors for detecting the presence and measuring the concentration of analytes in a sample. The microband electrodes of the invention have both a width and a thickness of microscopic dimensions. Preferably the width and thickness of the microband electrodes are less than the diffusion length of the analyte(s) of interest. In general, both the thickness and width of the electrodes are less than about 25 micrometers. The electrodes are separated by a gap insulating material that is large enough that the diffusion layers of the electrodes do not overlap such that there is no interference and the currents at the electrodes are additive. Microband electrode arrays of this invention exhibit true steady-state amperometric behavior.

37 Claims, 17 Drawing Sheets



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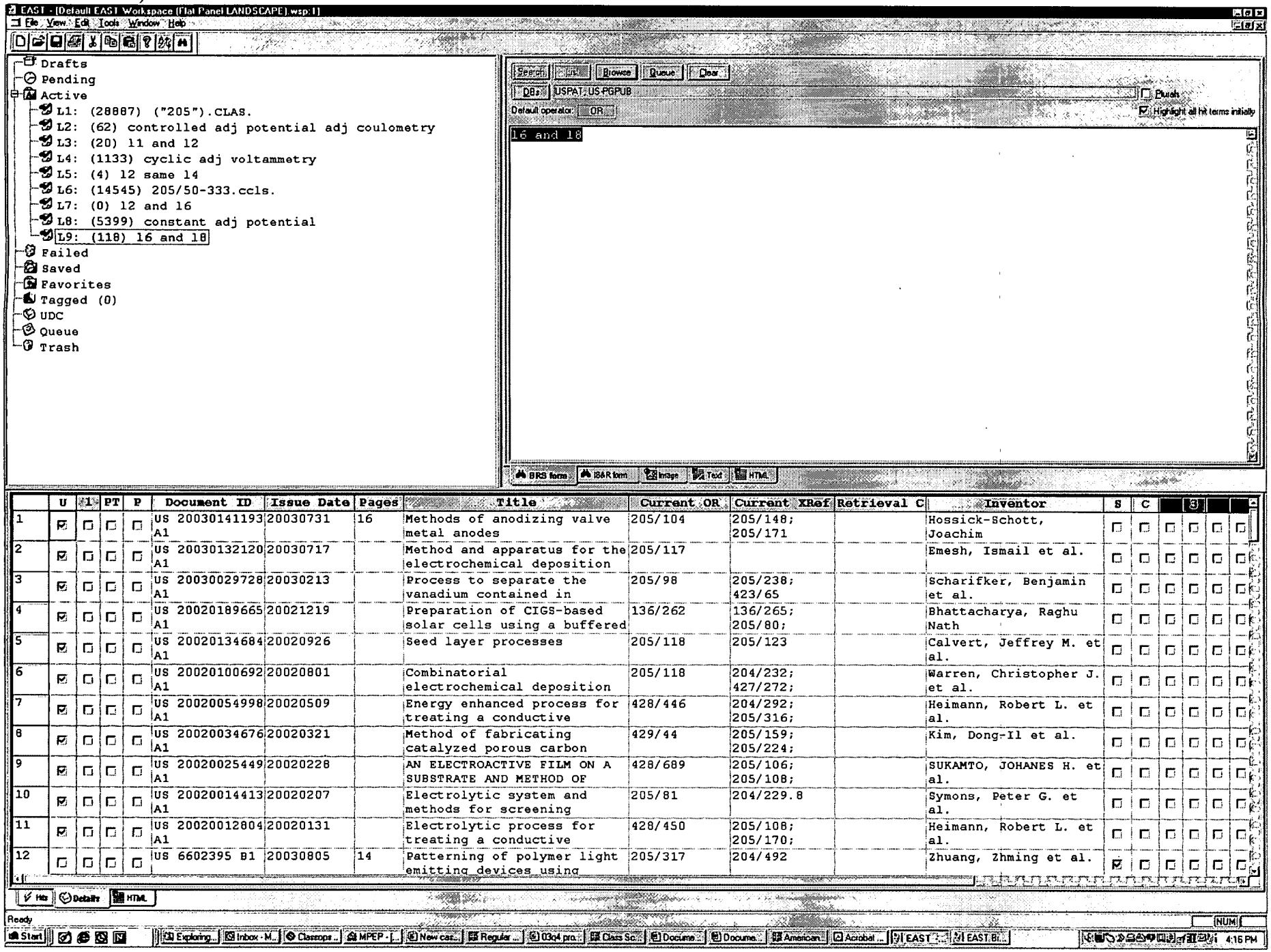

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2	☑	☐	☐	☐	US 20030132120 A1	20030717		Method and apparatus for the electrochemical deposition	205/117			Emesh, Ismail et al.	☐	☐	☐
3	☑	☐	☐	☐	US 20030029728 A1	20030213		Process to separate the vanadium contained in	205/98	205/238; 423/65		Scharifker, Benjamin et al.	☐	☐	☐
4	☑	☐	☐	☐	US 20020189665 A1	20021219		Preparation of CIGS-based solar cells using a buffered	136/262	136/265; 205/80;		Bhattacharya, Raghu Nath	☐	☐	☐
5	☑	☐	☐	☐	US 20020134684 A1	20020926		Seed layer processes	205/118	205/123		Calvert, Jeffrey M. et al.	☐	☐	☐
6	☑	☐	☐	☐	US 20020100692 A1	20020801		Combinatorial electrochemical deposition	205/118	204/232; 427/272;		Warren, Christopher J. et al.	☐	☐	☐
7	☑	☐	☐	☐	US 20020054998 A1	20020509		Energy enhanced process for treating a conductive	428/446	204/292; 205/316;		Heimann, Robert L. et al.	☐	☐	☐
8	☑	☐	☐	☐	US 20020034676 A1	20020321		Method of fabricating catalyzed porous carbon	429/44	205/159; 205/224;		Kim, Dong-Il et al.	☐	☐	☐
9	☑	☐	☐	☐	US 20020025449 A1	20020228		AN ELECTROACTIVE FILM ON A SUBSTRATE AND METHOD OF	428/689	205/106; 205/108;		SUKAMTO, JOHANES H. et al.	☐	☐	☐
10	☑	☐	☐	☐	US 20020014413 A1	20020207		Electrolytic system and methods for screening	205/81	204/229.8		Symons, Peter G. et al.	☐	☐	☐
11	☑	☐	☐	☐	US 20020012804 A1	20020131		Electrolytic process for treating a conductive	428/450	205/108; 205/170;		Heimann, Robert L. et al.	☐	☐	☐
12	☐	☐	☐	☐	US 6602395 B1	20030805	14	Patterning of polymer light emitting devices using	205/317	204/492		Zhuang, Zhming et al.	☑	☐	☐

EAST Browser - L9: (110) 6 and 8 | US 6309969 B1 | Tag: S | Doc: 14/110 (SORTED) | Format : KWIC

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	Document ID	Pages	1	3	U	S	C	P	Kind Codes	Sou
8	US 6375821 B1	12								USPAT
9	US 6338780 B1	20								USPAT
10	US 6332967 B1	19								USPAT
11	US 6325911 B1	10								USPAT
12	US 6322687 B1	20								USPAT
13	US 6319387 B1	17								USPAT
14	US 6309969 B1	13								USPAT

US-PAT-NO: 6309969

DOCUMENT-IDENTIFIER: US 6309969 B1

TITLE: Copper metallization structure and method of construction

---------- KWIC ---------

Detailed Description Text - DETX (9):

Because the first and second applied voltages are substantially maintained at constant or controlled voltage levels during copper film deposition in accordance with a preferred embodiment of the invention, the current may vary during the process. An alternative to this construction is to utilize during both the first and second phases a constant or controlled current method for deposition of the copper film. In this embodiment, the current is kept constant while the potential is allowed to fluctuate in range dependent upon the concentration of copper ions in the bath. Constant current electrochemical deposition produces a linear relationship between time and film thickness. Therefore, this method may preferred as it allows the thickness of the copper film to be easily controlled by setting the duration of the application of the current.

Current US Cross Reference Classification - CCXR (1):

205/291

(12) **United States Patent**
Oskam et al.

(10) **Patent No.: US 6,309,969 B1**
(45) **Date of Patent: Oct. 30, 2001**

(54) **COPPER METALLIZATION STRUCTURE AND METHOD OF CONSTRUCTION**

(75) Inventors: **Gerko Oskam**; **Peter C. Searson**; **Philippe M. Vereecken**; **John G. Long**; **Peter M. Hoffmann**, all of Baltimore, MD (US)

(73) Assignee: **The John Hopkins University**, Baltimore, MD (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: 09/184,579

(22) Filed: Nov. 3, 1998

(51) Int. Cl.[7] H01L 21/44

(52) U.S. Cl. 438/687; 205/291; 205/497; 205/574

(58) Field of Search 438/687; 205/291, 205/292, 497, 498, 507, 508, 574, 575

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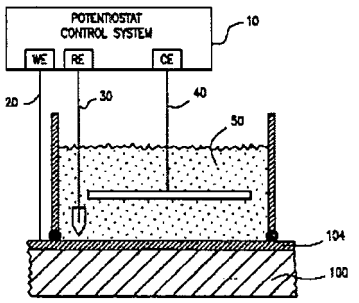
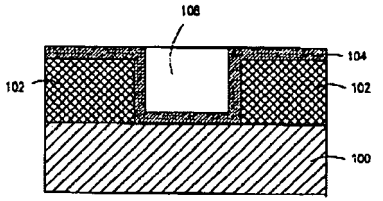
Primary Examiner—Olik Chaudhuri
Assistant Examiner—Ginette Peralta
(74) *Attorney, Agent, or Firm*—Dickstein Shapiro Morin & Oshinsky LLP

(57) **ABSTRACT**

The invention is directed to the use of copper as via and interconnect structures for an integrated circuit. The process in accordance with a preferred embodiment produces an interconnect layer of continuous copper with superior adhesion while requiring only a minimum number of steps for its production. This process addresses the current need in semiconductor manufacturing for reliable and performance-oriented vias and interconnect structures, while not being susceptible to many of the problems which plague the use of aluminum for similar structures. Fabrication of an integrated circuit in accordance with a preferred embodiment of the invention begins with the formation of semiconductor devices on a silicon wafer. Next, an intermetallic dielectric layer (IDL) is formed by materials such as silicon dioxide (SiO_2), polymide, or silicon nitride over the devices. This step is followed by the laying of a diffusion barrier layer on the IDL surface. The resulting product is then exposed to an electrochemical deposition or electroplating stage for the formation of a copper layer directly on top of the diffusion barrier layer. In accordance with a preferred embodiment of the invention, a variable voltage is applied to the electrochemical process in two different stages. The first stage produces nucleation of a high density of clusters and the second stage permits diffusion limited growth of the clusters so as to produce a continuous copper film layer.

15 Claims, 6 Drawing Sheets





EAST Browser - L9: [118] G and 8 | US 6319387 B1 | Tag: S | Doc: 13/118 (SORTED) | Format : KWIC

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8	US 6375821 B1	12							☑				USPAT
9	US 6338780 B1	20							☑				USPAT
10	US 6332967 B1	19							☑				USPAT
11	US 6325911 B1	10							☑				USPAT
12	US 6322687 B1	20							☑				USPAT
13	US 6319387 B1	17							☑				USPAT

US-PAT-NO: 6319387

DOCUMENT-IDENTIFIER: US 6319387 B1

TITLE: Copper alloy electroplating bath for microelectronic applications

---------- KWIC ---------

Detailed Description Text - DETX (15):
With the foregoing solution, it is possible to use a wide range of plating parameters to deposit a copper-zinc alloy layer 40 having a low resistivity (e.g., 1.8-2.4 u-ohms/cm) while also having the desired oxidation resistance and copper confinement properties. Preferably, the alloy is plated using a constant potential (as opposed to a constant current) waveform. The plating potential used is preferably between 300 mV and 900 mV cathodic. Although a DC plating waveform may be used, it is preferable to have a forward pulsed waveform. The forward pulsed waveform may have an on/off cycle of 50/20 msec to 90/10 msec. Particularly good via and trench microstructure tilling, results when a waveform of 0.6/0.3 msec is used.

Current US Original Classification - CCOR (1):
205/240

Current US Cross Reference Classification - CCXR (1):
205/106

Current US Cross Reference Classification - CCXR (2):
205/123

Current US Cross Reference Classification - CCXR (3):
205/239

(12) **United States Patent**
Krishnamoorthy et al.

(10) **Patent No.: US 6,319,387 B1**
(45) **Date of Patent: Nov. 20, 2001**

(54) **COPPER ALLOY ELECTROPLATING BATH FOR MICROELECTRONIC APPLICATIONS**

(75) Inventors: **Ahila Krishnamoorthy**, Menands; **David J. Duquette**, Loudonville; **Shyam P. Murarka**, Clifton Park, all of NY (US)

(73) Assignee: **Semitool, Inc.**, Kalispell, MT (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/386,772**

(22) Filed: **Aug. 31, 1999**

Related U.S. Application Data

(63) Continuation of application No. PCT/US99/14939, filed on Jun. 30, 1999.
(60) Provisional application No. 60/091,691, filed on Jun. 30, 1998, and provisional application No. 60/114,512, filed on Dec. 31, 1998.

(51) **Int. Cl.**[7] **C25D 3/58**
(52) **U.S. Cl.** **205/240**; 205/106; 205/123; 205/239
(58) **Field of Search** 205/239, 240, 205/241, 242, 104, 123; 106/1.23, 1.26

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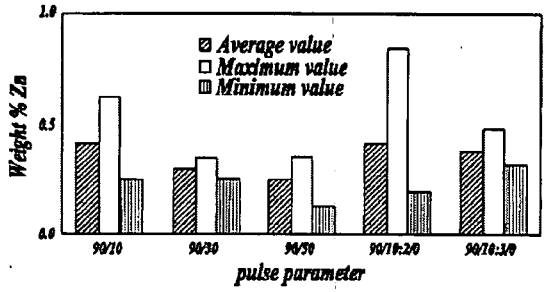
Primary Examiner—Kathryn Gorgos
Assistant Examiner—William T. Leader
(74) *Attorney, Agent, or Firm*—Christensen O'Connor Johnson Kindness PLLC

(57) **ABSTRACT**

A metallized structure for use in a microelectronic circuit is set forth. The metallized structure comprises a dielectric layer, an ultra-thin film bonding layer disposed exterior to the dielectric layer, and a low-Me concentration, copper-Me alloy layer disposed exterior to the ultra-thin film bonding layer. The Me is a metal other than copper and, preferably, is zinc. The concentration of the Me is less than about 5 atomic percent, preferably less than about 2 atomic percent, and even more preferably, less than about 1 atomic percent. In a preferred embodiment of the metallized structure, the dielectric layer, ultra-thin film bonding layer and the copper-Me alloy layer are all disposed immediately adjacent one another. If desired, a primary conductor, such as a film of copper, may be formed exterior to the foregoing layer sequence. The present invention also contemplates methods for forming the foregoing structure as well as electroplating baths that may be used to deposit the copper-Me alloy layer.

12 Claims, 10 Drawing Sheets



EAST Browser - L9: [10] 6 and 8 | US 6332967 B1 | Tag: 5 | Doc: 10/10 [SORTED] | Format: KWIC

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5	US 6468806 B1	19								USPAT
6	US 6468690 B1	11								USPAT
7	US 6387243 B1	12								USPAT
8	US 6375821 B1	12								USPAT
9	US 6338780 B1	20								USPAT
10	US 6332967 B1	19								USPAT
11	US 6325911 B1	10								USPAT

US-PAT-NO: 6332967

DOCUMENT-IDENTIFIER: US 6332967 B1

TITLE: Electro-deposition of superconductor oxide films

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Detailed Description Text - DETX (27):
The electrodeposition was performed in a closed-cell configuration at 24.degree. C. using a conventional three-electrode cell, where the reference electrode was Ag (pseudo-reference), the counter electrode was a Pt gauze, and the substrate (i.e., the working) electrode was a single crystal LaAlO.sub.3 (LAO) coated with 300 .ANG. Ag. The films were electroplated by using a constant potential of -3V. All samples were deposited in a vertical cell, where the electrodes (substrate, counter, and reference) were suspended vertically from the top of the cell. All chemicals were of Analar or Puratronic-grade purity and were used as received. A Princeton Applied Research potentiostat/galvanostat Model 273A with an IBM PC AT computer interface was used for controlling the pulsed-potential electrolysis and to monitor the current and voltage profiles.

Current US Original Classification - CCOR (1):
205/51

Current US Cross Reference Classification - CCXR (1):
205/170

Current US Cross Reference Classification - CCXR (2):
205/186

Current US Cross Reference Classification - CCXR (3):
205/227

(12) **United States Patent**
Bhattacharya

(10) **Patent No.: US 6,332,967 B1**
(45) **Date of Patent: Dec. 25, 2001**

(54) **ELECTRO-DEPOSITION OF SUPERCONDUCTOR OXIDE FILMS**

(75) Inventor: **Raghu N. Bhattacharya**, Littleton, CO (US)

(73) Assignee: **Midwest Research Institute**, Kansas City, MO (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/448,612**

(22) Filed: **Nov. 23, 1999**

(51) Int. Cl.[7] C25D 7/00; C25D 5/10; C23C 28/02

(52) U.S. Cl. 205/51; 205/170; 205/186; 205/227; 505/472; 505/500; 505/501; 505/510

(58) Field of Search 205/170, 186, 205/227, 51; 505/472, 500, 501, 510, 470; 427/372.2; 148/96

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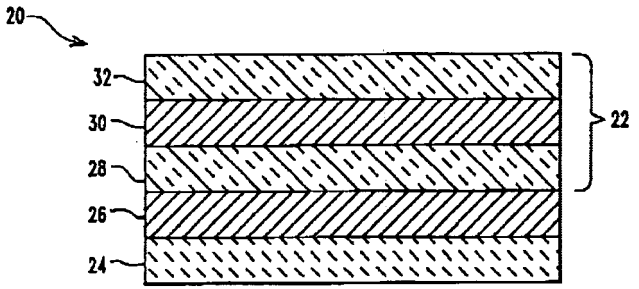
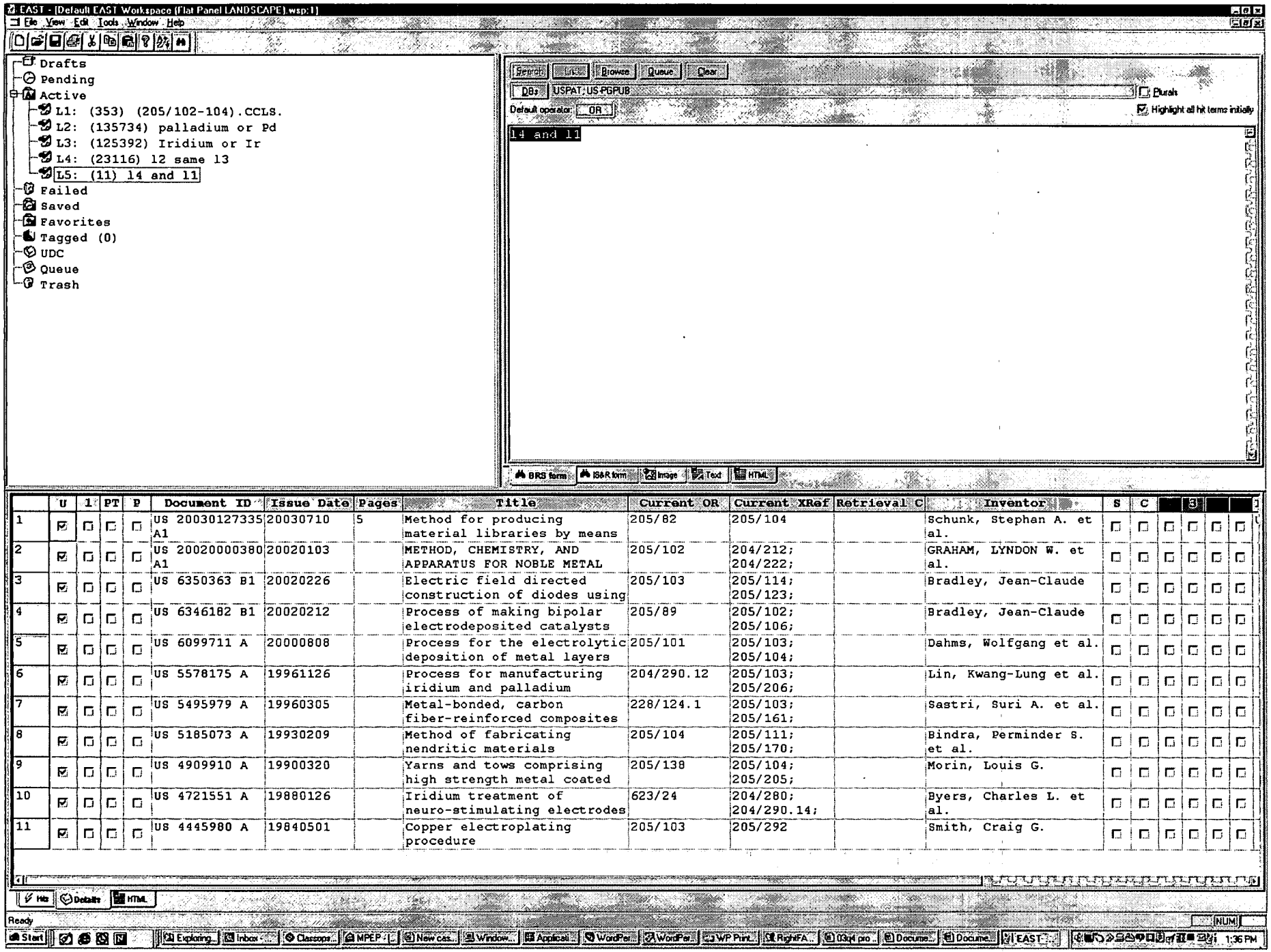
Primary Examiner—Edna Wong
(74) *Attorney, Agent, or Firm*—Paul J. White

(57) **ABSTRACT**

Methods for preparing high quality superconducting oxide precursors which are well suited for further oxidation and annealing to form superconducting oxide films. The method comprises forming a multilayered superconducting precursor on a substrate by providing an electrodeposition bath comprising an electrolyte medium and a substrate electrode, and providing to the bath a plurality of precursor metal salts which are capable of exhibiting superconducting properties upon subsequent treatment. The superconducting precursor is then formed by electrodepositing a first electrodeposited (ED) layer onto the substrate electrode, followed by depositing a layer of silver onto the first electrodeposited (ED) layer, and then electrodepositing a second electrodeposited (ED) layer onto the Ag layer. The multilayered superconducting precursor is suitable for oxidation at a sufficient annealing temperature in air or an oxygen-containing atmosphere to form a crystalline superconducting oxide film.

30 Claims, 9 Drawing Sheets





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1	☑	☐	☐	☐	US 20030127335 A1	20030710	5	Method for producing material libraries by means	205/82	205/104		Schunk, Stephan A. et al.	☐	☐
2	☑	☐	☐	☐	US 20020000380 A1	20020103		METHOD, CHEMISTRY, AND APPARATUS FOR NOBLE METAL	205/102	204/212; 204/222;		GRAHAM, LYNDON W. et al.	☐	☐
3	☑	☐	☐	☐	US 6350363 B1	20020226		Electric field directed construction of diodes using	205/103	205/114; 205/123;		Bradley, Jean-Claude	☐	☐
4	☑	☐	☐	☐	US 6346182 B1	20020212		Process of making bipolar electrodeposited catalysts	205/89	205/102; 205/106;		Bradley, Jean-Claude	☐	☐
5	☑	☐	☐	☐	US 6099711 A	20000808		Process for the electrolytic deposition of metal layers	205/101	205/103; 205/104;		Dahms, Wolfgang et al.	☐	☐
6	☑	☐	☐	☐	US 5578175 A	19961126		Process for manufacturing iridium and palladium	204/290.12	205/103; 205/206;		Lin, Kwang-Lung et al.	☐	☐
7	☑	☐	☐	☐	US 5495979 A	19960305		Metal-bonded, carbon fiber-reinforced composites	228/124.1	205/103; 205/161;		Sastri, Suri A. et al.	☐	☐
8	☑	☐	☐	☐	US 5185073 A	19930209		Method of fabricating nendritic materials	205/104	205/111; 205/170;		Bindra, Perminder S. et al.	☐	☐
9	☑	☐	☐	☐	US 4909910 A	19900320		Yarns and tows comprising high strength metal coated	205/138	205/104; 205/205;		Morin, Louis G.	☐	☐
10	☑	☐	☐	☐	US 4721551 A	19880126		Iridium treatment of neuro-stimulating electrodes	623/24	204/280; 204/290.14;		Byers, Charles L. et al.	☐	☐
11	☑	☐	☐	☐	US 4445980 A	19840501		Copper electroplating procedure	205/103	205/292		Smith, Craig G.	☐	☐

EAST Browser - L5: (11) 4 and 1 | US 6346182 B1 | Tag: 5 | Doc: 2/11 (SORTED) | Format : KWIC

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3	US 6099711 A	13			☑					USPAT
4	US 5578175 A	12			☑					USPAT
5	US 5495979 A	9			☑					USPAT
6	US 5185073 A	15			☑					USPAT
7	US 4909910 A	8			☑					USPAT

US-PAT-NO: 6346182

DOCUMENT-IDENTIFIER: US 6346182 B1

TITLE: Process of making bipolar electrodeposited catalysts and catalysts so made

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Brief Summary Text - BSTX (15):
One electrodeposition tactic that avoids electrical contact with the conductive support is photoelectrodeposition onto semiconductive particles. This has been used extensively as a method of electrodepositing catalytically active metals (e.g. Au, Pt, Pd, Ag, Rh, Ir) onto a dispersed semiconducting support (e.g. TiO.sub.2, ZnO, SnO.sub.2, ZrO.sub.2, ThO.sub.2, CdS, WO.sub.3). In this case photons promote electrons from the valence band into the conduction band of the semiconducting particles, creating a situation where anodic and cathodic processes occur on different regions of the same particle. Although this method has been successful in producing catalysts, it requires the use of a semiconductor with a bandgap tuned to the wavelengths capable of penetrating into the sample. Furthermore, due to absorption of light, homogeneous exposures within large volumes is not possible without prolonged mixing.

Detailed Description Text - DETX (14):
The conductive form of carbon may be graphite or known forms of conductive diamond. Graphite is preferred. Preferred metals may be Pt, Au, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, W, Re, Os, Ir, Hg, Tl, Pb or Bi and alloys, conductive metal oxides or mixtures thereof. Non-limiting examples of suitable conductive polymers include polypyrrole and its derivatives, polyaniline and its derivatives or polythiophene and its derivatives. A non-limiting example among suitable conductive salt crystal material is a tetrathiafulvene salt. A "conductive semiconductor", as used herein, is one which has sufficient electrically conductive properties to be capable of bipolar polarization using the process of this invention. A conductive semiconductor material preferably comprises doped Si or Ge, or elements of the Periodic Table Groups III and V, such as GaAs, GaP, InP, or elements from the Periodic Table Groups II and VI, such as CdS, CdSe, CdTe, ZnS, ZnSe, ZnTe, HgS, HgSe or HgTe, for example.

Detailed Description Text - DETX (22):
The source of the catalytic substance is preferably a salt or salts containing an ion of Pd, Pt, Ag, Au, Ni, Cu, Co, Fe, Ru, Rh, Cr, Mn, Ir, Os, Re, Zr, Mo, Ti, In, Sn, Hg, Tl, Pb, Bi, Cd, Ce and or mixtures of them. Particularly preferred are salts of Pd, Pt, Rh, Ag, Au, Co, Fe, and Cu, due to their recognized catalytic properties.

Detailed Description Text - DETX (32):
Preferably, the electrodes are comprised of metals or conductive metal oxides of the following group: graphite, Pt, Au, Al, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr, Nb, Mo, Tc, Ru, Rh, Pd, Ag, Cd, In, Sn, W, Re, Os, Ir, Hg, Tl, Pb, or Bi, or alloys or mixtures of them. Graphite and platinum are the more

(12) **United States Patent**
Bradley

(10) **Patent No.: US 6,346,182 B1**
(45) **Date of Patent: Feb. 12, 2002**

(54) **PROCESS OF MAKING BIPOLAR ELECTRODEPOSITED CATALYSTS AND CATALYSTS SO MADE**

(75) Inventor: **Jean-Claude Bradley**, Philadelphia, PA (US)

(73) Assignee: **Drexel University**, Philadelphia, PA (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **09/667,272**

(22) Filed: **Sep. 22, 2000**

Related U.S. Application Data

(63) Continuation of application No. PCT/US99/06430, filed on Mar. 24, 1999.
(60) Provisional application No. 60/079,144, filed on Mar. 24, 1998.

(51) Int. Cl.[7] **C25D 5/00**
(52) U.S. Cl. 205/89; 205/102; 205/106; 205/109
(58) Field of Search 205/89, 102, 105, 205/109

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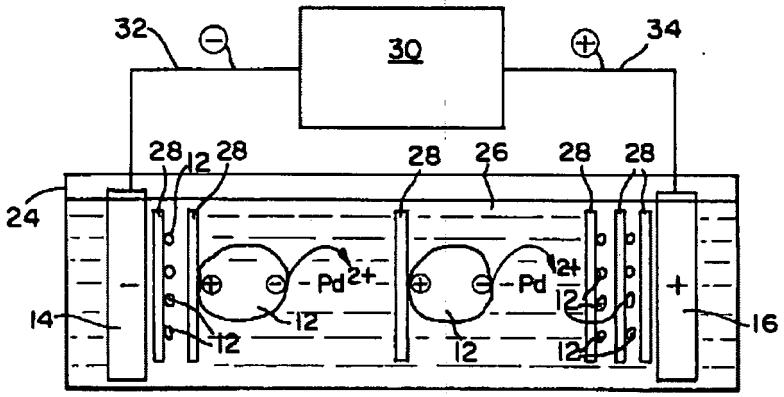
Primary Examiner—Kishor Mayekar
(74) *Attorney, Agent, or Firm*—Akin, Gump, Strauss, Hauer & Feld, L.L.P.

(57) **ABSTRACT**

This invention relates to a bipolar electrochemical process for toposelective electrodeposition of a catalytic substance on an electrically conductive particulate substrate to produce a catalyst, as well as to the catalyst so produced. The process comprises: (a) placing the conductive particulate substrate and a source of the catalytic substance into an environment capable of conducting electricity; (b) aligning the conductive particulate substrate on which the catalytic substance is to be deposited with respect to an electric field such that the conductive particulate substrate is not in physical contact with electrodes and such that the catalytic substance will be deposited in a predetermined location on the particulate substrate when an electric field is applied; and (c) creating an electric field of a sufficient strength and for a time sufficient to deposit the catalytic substance from the source of the catalytic substance on the conductive particulate substrate at the predetermined location in substantial alignment with the electric field.

25 Claims, 4 Drawing Sheets



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1	US 6350363 B1	13							☑				USPAT
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6	US 5185073 A	15						☑					USPAT
7	US 4909910 A	8						☑					USPAT

Claims Text - CLTX (1):
1. A process for manufacturing iridium and palladium oxides-coated titanium electrode comprising the steps of:

Claims Text - CLTX (3):
(b) applying iridium and palladium compounds to said titanium substrate to form an iridium and palladium containing layer by a cyclic voltametric deposition process; and

Claims Text - CLTX (4):
(c) heat-treating said iridium and palladium-applied titanium substrate to obtain an iridium and palladium oxides-coated titanium electrode.

Claims Text - CLTX (5):
2. A process as claimed in claim 1, wherein said step (b) is executed by immersing said titanium substrate in an iridium and palladium-containing solution to obtain said iridium and palladium containing layer on said titanium substrate by said cyclic voltametric deposition process in said iridium and palladium-containing solution.

Claims Text - CLTX (6):
3. A process as claimed in claim 2, wherein said iridium and palladium-containing solution comprises a solution of K.sub.2 IrCl.sub.6, PdCl.sub.2, K.sub.2 SO.sub.4 and HCl.

Claims Text - CLTX (8):
5. A process as claimed in claim 2, wherein said iridium and palladium-containing solution has a pH value of about 1.2.

Claims Text - CLTX (43):
35. An iridium and palladium oxides-applied titanium electrode manufactured by a process as claimed in claim 1, comprising:

Claims Text - CLTX (45):
(2) an iridium and palladium oxides layer deposited to said titanium substrate.

Current US Cross Reference Classification - CCXR (1):
205/103

Other Reference Publication - OREF (10):
J. Electroanal. Chem., vol. 256, 1988, pp. 199-205, J. Cox et al., "Modification of Glassy Carbon With a Stable Film Containing Iridium Oxide and Palladium" no month available.

United States Patent [19]

Lin et al.

[11] **Patent Number: 5,578,175**

[45] **Date of Patent: Nov. 26, 1996**

[54] **PROCESS FOR MANUFACTURING IRIDIUM AND PALLADIUM OXIDES-COATED TITANIUM ELECTRODE AND THE ELECTRODE PRODUCED THEREBY**

[75] Inventors: **Kwang-Lung Lin; Ju-Tung Lee; Yuan-Po Lee, all of Tainan, Taiwan**

[73] Assignee: **National Science Council, Taipei, Taiwan**

[21] Appl. No.: **291,452**

[22] Filed: **Aug. 16, 1994**

[51] Int. Cl.[6] **C25B 11/10; C25D 5/00; C25D 5/18**

[52] U.S. Cl. ..... **204/290 F; 205/224; 205/82; 205/83; 205/220; 205/206; 205/210; 205/211; 205/212; 205/103; 205/227**

[58] Field of Search ..... **204/290 R, 192.1, 204/192.11; 205/96, 102, 103, 206, 82, 83, 212, 257, 224, 229, 333, 227, 210, 211; 427/123, 725, 126.5, 226, 327, 328, 383.1, 383.7**

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(List continued on next page.)

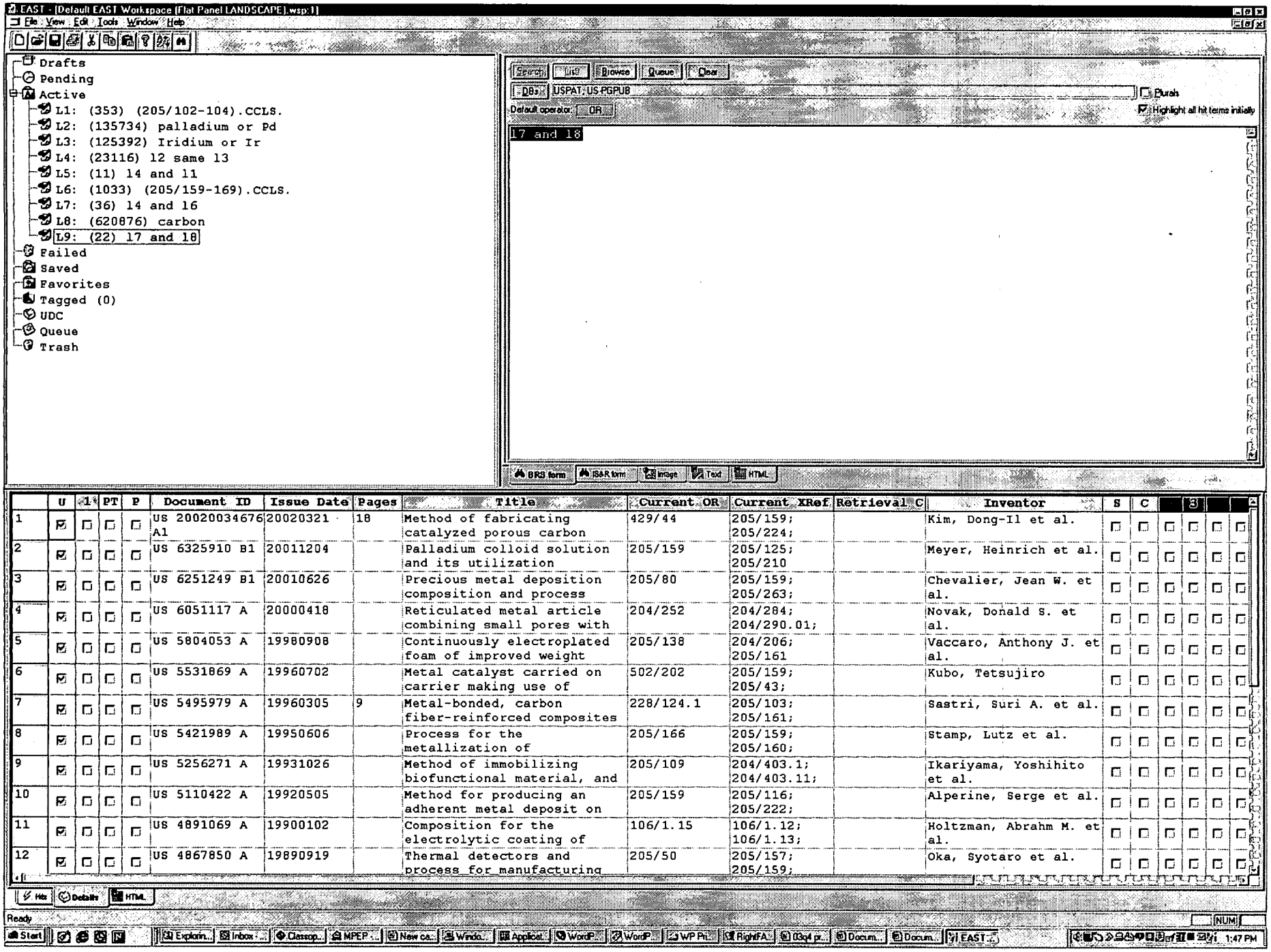
Primary Examiner—Kathryn Gorgos

Attorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neustadt, P.C.

[57] **ABSTRACT**

A process for manufacturing an iridium and palladium oxides-coated titanium electrode comprises preparing a titanium substrate having a surface, applying iridium and palladium to be formed on the surface of the titanium substrate, and heat-treating the iridium and palladium oxides-applied titanium substrate to obtain an iridium and palladium oxides-coated titanium electrode. This invention provides a process for obtaining a coated titanium electrode having therein a good adhesion between the coating material and the titanium electrode, and having an excellent electrochemical stability and a superior catalytic activity in an acidic environment.

35 Claims, 5 Drawing Sheets



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1	☑	☐	☐	☐	US 20020034676 A1	20020321	18	Method of fabricating catalyzed porous carbon	429/44	205/159; 205/224;		Kim, Dong-Il et al.	☐	☐	☐
2	☑	☐	☐	☐	US 6325910 B1	20011204		Palladium colloid solution and its utilization	205/159	205/125; 205/210		Meyer, Heinrich et al.	☐	☐	☐
3	☑	☐	☐	☐	US 6251249 B1	20010626		Precious metal deposition composition and process	205/80	205/159; 205/263;		Chevalier, Jean W. et al.	☐	☐	☐
4	☑	☐	☐	☐	US 6051117 A	20000418		Reticulated metal article combining small pores with	204/252	204/284; 204/290.01;		Novak, Donald S. et al.	☐	☐	☐
5	☑	☐	☐	☐	US 5804053 A	19980908		Continuously electroplated foam of improved weight	205/138	204/206; 205/161		Vaccaro, Anthony J. et al.	☐	☐	☐
6	☑	☐	☐	☐	US 5531869 A	19960702		Metal catalyst carried on carrier making use of	502/202	205/159; 205/43;		Kubo, Tetsujiro	☐	☐	☐
7	☑	☐	☐	☐	US 5495979 A	19960305	9	Metal-bonded, carbon fiber-reinforced composites	228/124.1	205/103; 205/161;		Sastri, Suri A. et al.	☐	☐	☐
8	☑	☐	☐	☐	US 5421989 A	19950606		Process for the metallization of	205/166	205/159; 205/160;		Stamp, Lutz et al.	☐	☐	☐
9	☑	☐	☐	☐	US 5256271 A	19931026		Method of immobilizing biofunctional material, and	205/109	204/403.1; 204/403.11;		Ikariyama, Yoshihito et al.	☐	☐	☐
10	☑	☐	☐	☐	US 5110422 A	19920505		Method for producing an adherent metal deposit on	205/159	205/116; 205/222;		Alperine, Serge et al.	☐	☐	☐
11	☑	☐	☐	☐	US 4891069 A	19900102		Composition for the electrolytic coating of	106/1.15	106/1.12; 106/1.13;		Holtzman, Abrahm M. et al.	☐	☐	☐
12	☑	☐	☐	☐	US 4867850 A	19890919		Thermal detectors and process for manufacturing	205/50	205/157; 205/159;		Oka, Syotaro et al.	☐	☐	☐

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5	US 5804053 A	13								USPAT
6	US 5531869 A	18								USPAT
7	US 5495979 A	9								USPAT
8	US 5421989 A	11								USPAT
9	US 5256271 A	21								USPAT
10	US 5110422 A	7								USPAT

US-PAT-NO: 5110422

DOCUMENT-IDENTIFIER: US 5110422 A

TITLE: Method for producing an adherent metal deposit on carbon, and mirror obtained by this method

---------- KWIC ---------

Abstract Text - ABTX (1):
A surface layer of a material containing carbon and/or a carbide is produced on the outer surface of a solid carbon-based substrate (1) by selective application of material, said surface layer adhering strongly to the substrate, having a high specific surface area and having open pores (5) of a depth of at least 1 nm, and a metal material having a strong affinity for carbon, comprising at least one metal chosen from cerium, cobalt, chromium, iron, hafnium, iridium, osmium, palladium, platinum, rhodium, ruthenium, lanthanum, manganese, molybdenum, nickel, silicon, tantalum, thorium, titanium, uranium and tungsten, is deposited on said surface layer, substantially filling said pores.

TITLE - TI (1):
Method for producing an adherent metal deposit on carbon, and mirror obtained by this method

Brief Summary Text - BSTX (1):
The invention relates to a method for producing a metal deposit on a solid carbon-based substrate, in particular the production of mirrors of low inertia, more particularly for powerful laser beams.

Brief Summary Text - BSTX (2):
A carbon-based substrate is here understood to be a substrate formed either from a material comprising at least 50% by weight of uncombined carbon or a composite material formed from a disperse phase and a matrix comprising at least 50% by weight of uncombined carbon.

Brief Summary Text - BSTX (5):
However, in the experience of the authors of the present invention, the adherence of any metal on graphite is a very difficult problem which the document under consideration provides no means of solving. An excellent adherence of the coating is necessary, on the one hand to enable mechanical machining of said coating without it tearing away and on the other hand so that the mirror withstands variations in temperature and the high temperature gradients due to the incidence of powerful rays, taking account of the difference between the coefficient of thermal expansion of carbon and those of the metals, which is very great even when the grade of graphite is chosen so as to limit it, as proposed in the prior application.

Brief Summary Text - BSTX (6):
The aim of the invention is to provide a method enabling a metal deposit to

US005110422A

United States Patent [19]

Alperine et al.

[11] **Patent Number: 5,110,422**

[45] **Date of Patent: May 5, 1992**

[54] **METHOD FOR PRODUCING AN ADHERENT METAL DEPOSIT ON CARBON, AND MIRROR OBTAINED BY THIS METHOD**

[75] Inventors: Serge Alperine, Paris; Pierre Josso, Issy Les Moulineaux, both of France

[73] Assignee: Office National D'Etudes et de Recherches Aerospatiales, Bagneux, France

[21] Appl. No.: 626,593

[22] Filed: Dec. 12, 1990

[30] Foreign Application Priority Data

Dec. 13, 1989 [FR] France 89 16486

[51] Int. Cl.[5] C25D 7/08

[52] U.S. Cl. 205/189; 427/419.7; 427/304; 427/162; 359/900; 359/883; 205/116; 205/222

[58] Field of Search 350/609, 610, 641; 427/228, 305, 404, 162, 419.7; 204/19, 38.1

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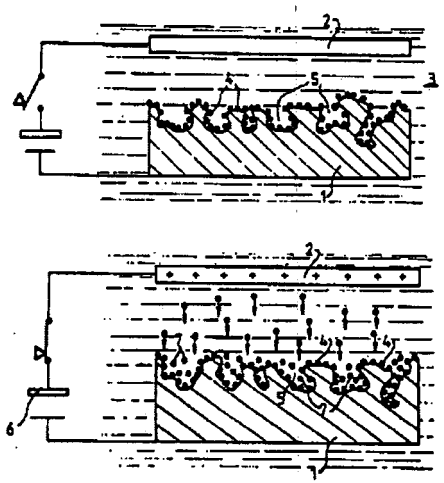
Primary Examiner—John Niebling
Assistant Examiner—Kishor Mayekar
Attorney, Agent, or Firm—Armstrong, Nikaido, Marmelstein, Kubovick & Murray

[57] ABSTRACT

A surface layer of a material containing carbon and/or a carbide is produced on the outer surface of a solid carbon-based substrate (1) by selective application of material, said surface layer adhering strongly to the substrate, having a high specific surface area and having open pores (5) of a depth of at least 1 nm, and a metal material having a strong affinity for carbon, comprising at least one metal chosen from cerium, cobalt, chromium, iron, hafnium, iridium, osmium, palladium, platinum, rhodium, ruthenium, lanthanum, manganese, molybdenum, nickel, silicon, tantalum, thorium, titanium, uranium and tungsten, is deposited on said surface layer, substantially filling said pores.

The metal deposit (6) may be rectified and polished without peeling off, in order to produce a mirror of low inertia.

15 Claims, 2 Drawing Sheets



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12	US 4867850 A	8				☑				USPAT
13	US 4680093 A	6				☑				USPAT
14	US 4673468 A	10				☑				USPAT
15	US 4661403 A	8				☑				USPAT
16	US 4643918 A	4				☑				USPAT
17	US 4517253 A	10				☑				USPAT

US-PAT-NO: 4517253

DOCUMENT-IDENTIFIER: US 4517253 A

TITLE: Cryoelectrodeposition

---------- KWIC ---------

Brief Summary Text - BSTX (2):
C. H. Lee and F. A. Kroger (J. Electrochem. Soc. 129 (5), 936-942, 1982) have electroplated amorphous silicon containing fluorine and carbon from solutions of K.sub.2 SiF.sub.6 in acetone with HF at ambient temperatures. These films were doped with boron or phosphorus.

Detailed Description Text - DETX (39):
Niobium was deposited from a solution of Nb(OCH.sub.2 CH.sub.3).sub.5 and (CH.sub.3)4NCl in a mixture of BF.sub.3 and HCl. The niobium deposits observed were highly conductive, thin layers with thicker dendritic regions up to ten micrometers in diameter. The estimated thickness of the deposit is one micrometer. Scanning Auger analysis (AES) revealed oxygen to be present as well. Some expansions and explanation of the foregoing are made in this paragraph. The ion soution used in the electrodeposition process is a liquid halogen (which generally includes liquid interhalogen, e.g., chlorine monofluoride) or a hydrogen halide such as hydrogen chloride to which is added a material which increases the anion concentration and enhances electrical conductivity. The solution is established at a temperature where the solvent is a liquid, as indicated above, e.g., between 110 degrees K. and 380 degrees K. Reactive materials that can be deposited on a substrate in accordance with the present teaching include, but are not restricted to, refractory metals taken from the group consisting of Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W or metalloids taken from the group consisting of Si, Ge, B, P, Ga and As. Other metals which may be deposited include ruthenium, osmium, rhodium, iridium, palladium, platinum, silver and gold. Other materials include silicides such as MoSi.sub.2 and WSi.sub.2 to provide a wear-resistant surface on the substrate. The product produced in according to the present teaching is totally free of thermal damage due to depositing of the material on the substrate, and the layer so deposited can be thicker than ten micrometers.

Claims Text - CLTX (20):
18. A method of electrodeposition according to claim 1 in which the substrate is composed of graphite, vitreous carbon or any other electrically conductive form of carbon.

Claims Text - CLTX (21):
19. A method of electrodeposition according to claim 1 in which the material to be electrodeposited is a noble or precious metal taken from the group consisting of ruthenium, osmium, rhodium, iridium, palladium, and platinum.

Claims Text - CLTX (42):
36. A product according to claim 35 wherein the electrolytically deposited

United States Patent [19]

Rose et al.

[11] **Patent Number: 4,517,253**

[45] **Date of Patent: May 14, 1985**

[54] **CRYOELECTRODEPOSITION**

[76] Inventors: Robert M. Rose, 18 Morgan St., Wenham, Mass. 01984; Donald R. Sadoway, 53 Vernon Rd., Belmont, Mass. 02178

[21] Appl. No.: 572,822

[22] Filed: Jan. 23, 1984

[51] Int. Cl.³ C25B 1/00

[52] U.S. Cl. 428/620; 428/637; 428/638; 428/641; 428/642; 428/646; 428/650; 428/653; 428/684; 204/58.5

[58] Field of Search ..... 204/58.5, 1 T, 228; 75/107; 428/620, 637, 638, 641, 642, 646, 650, 653, 684

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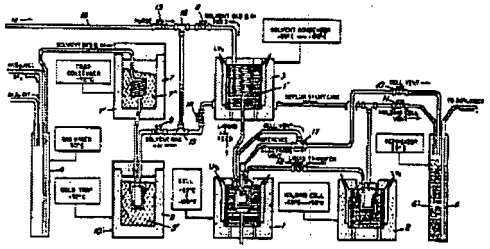
Primary Examiner—R. L. Andrews
Attorney, Agent, or Firm—Robert Shaw

[57] ABSTRACT

A process for electrodeposition of a material on a substrate that includes the steps of establishing a liquid halogenous electrolyte containing the material to be plated on the substrate and a solute, said electrolyte having an appropriate electrical conductance in a cryogenic environment; and establishing an electric field within the electrolyte to effect migration of ions of said material to the substrate where they deposit.

51 Claims, 3 Drawing Figures



EAST Browser - L9: (22) 7 and 8 | US 20020034676 A1 | Tag: S | Doc: 22/22 (SORTED) | Format : FULL

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17	US 4517253 A	10					☑				USPAT
18	US 4495046 A	8					☑				USPAT
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20	US 3930963 A	28					☑				USPAT
21	US 3865699 A	8					☑				USPAT
22	US 20020034676 A	18					☑				US-PG

PGPUB-DOCUMENT-NUMBER: 20020034676

PGPUB-FILING-TYPE: new

DOCUMENT-IDENTIFIER: US 20020034676 A1

TITLE: Method of fabricating catalyzed porous carbon electrode for fuel cell

PUBLICATION-DATE: March 21, 2002

INVENTOR-INFORMATION:

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Lee, Chang-Hyeong	Chungcheongbuk-do		KR	
Kim, Dong-Chun	Seoul		KR	

APPL-NO: 09/ 886620

DATE FILED: June 22, 2001

FOREIGN-APPL-PRIORITY-DATA:

COUNTRY	APPL-NO	DOC-ID	APPL-DATE
KR	2000-34783	2000KR-2000-34783	June 23, 2000

INT-CL: [07], H01M004/96 , H01M004/88 , C25D003/50

US-CL-PUBLISHED: 429/44, 502/101 , 205/159 , 205/224

US-CL-CURRENT: 429/44, 205/159 , 205/224 , 502/101

REFERENCE-FIGURES: 1

ABSTRACT:

Disclosed herein is a method of fabricating a catalyzed porous electrode for fuel cell, which electrode can be fabricated in a simple and easy manner without forming a catalyst support layer of carbon particles, and has an excellent, stable catalytic efficiency. The method comprises treating an electrically conductive, porous carbon substrate with an oxidizing agent; making one face of the porous carbon substrate in contact with an electrodeposition solution As containing ions of a catalytic metal; applying a pulsed potential to the electrodeposition solution to deposit the catalytic metal on the porous substrate, thereby catalyzing the porous substrate; and heat-treating the catalyzed porous substrate.

BRIEF SUMMARY:

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] The present invention relates in general to electrodes for fuel cells and a method of fabricating the same. More particularly, it relates to a method of fabricating catalyzed carbon electrodes for direct methanol fuel cells by electrodepositing catalysts directly on porous carbon substrates, and

(19) **United States**

(12) **Patent Application Publication** (10) **Pub. No.: US 2002/0034676 A1**

Kim et al. (43) **Pub. Date: Mar. 21, 2002**

(54) **METHOD OF FABRICATING CATALYZED POROUS CARBON ELECTRODE FOR FUEL CELL**

(76) Inventors: **Dong-Il Kim**, Chungcheongbuk-do (KR); **Chang-Hyeong Lee**, Chungcheongbuk-do (KR); **Dong-Chun Kim**, Seoul (KR)

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(21) Appl. No.: **09/886,620**

(22) Filed: **Jun. 22, 2001**

(30) **Foreign Application Priority Data**

Jun. 23, 2000 (KR) 2000-34783

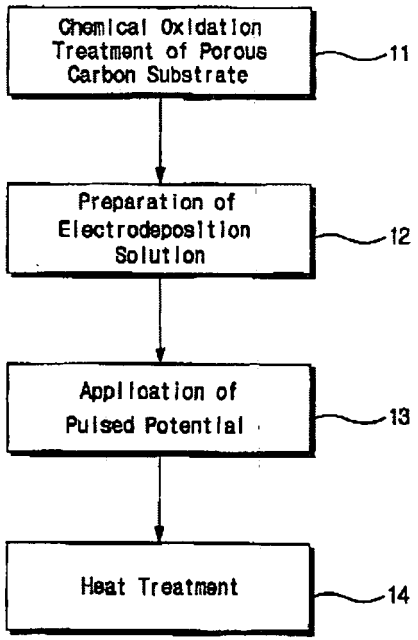
Publication Classification

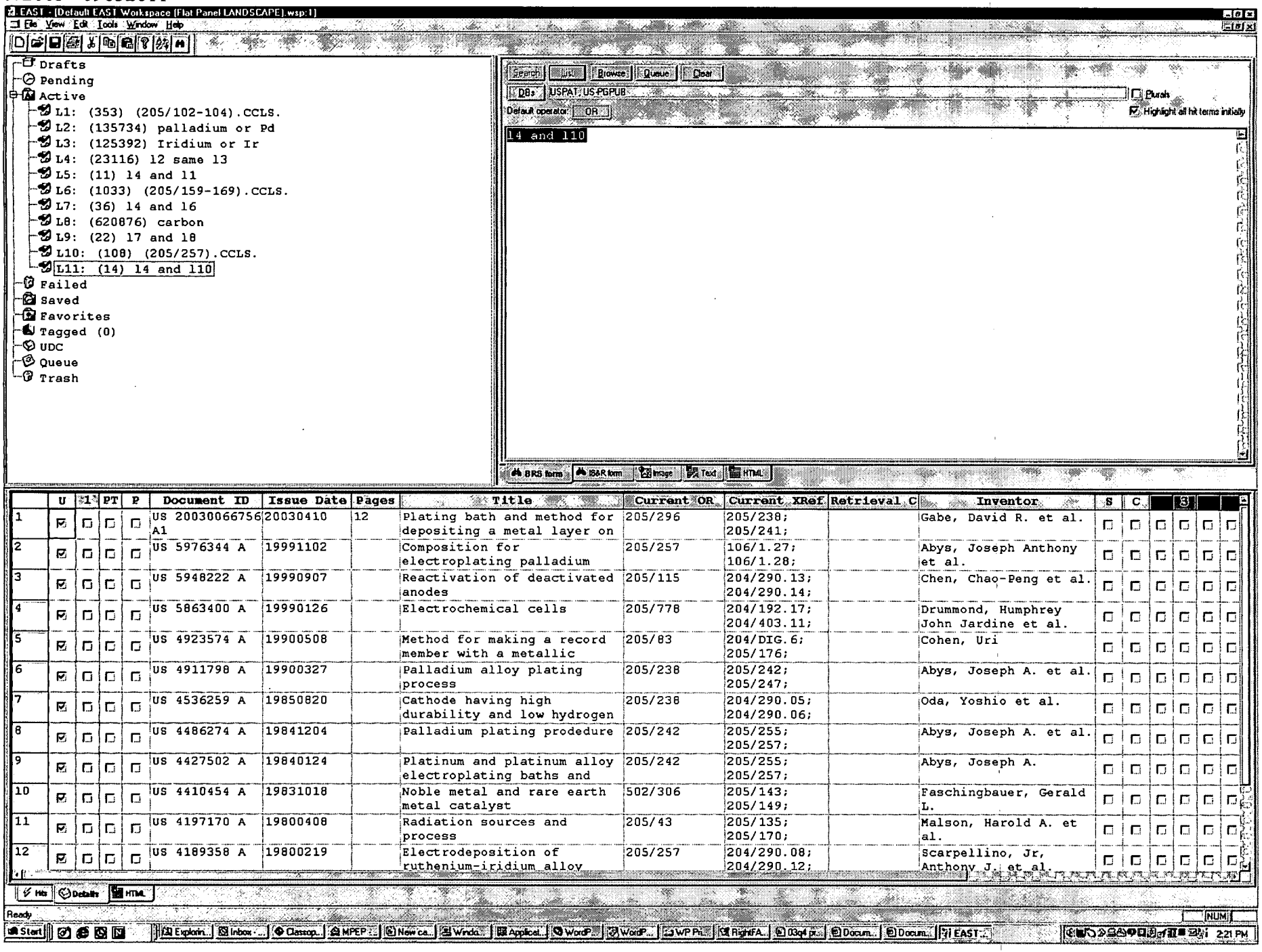
(51) Int. Cl.[7] H01M 4/96; H01M 4/88; C25D 3/50

(52) U.S. Cl. 429/44; 502/101; 205/159; 205/224

(57) **ABSTRACT**

Disclosed herein is a method of fabricating a catalyzed porous electrode for fuel cell, which electrode can be fabricated in a simple and easy manner without forming a catalyst support layer of carbon particles, and has an excellent, stable catalytic efficiency. The method comprises treating an electrically conductive, porous carbon substrate with an oxidizing agent; making one face of the porous carbon substrate in contact with an electrodeposition solution As containing ions of a catalytic metal; applying a pulsed potential to the electrodeposition solution to deposit the catalytic metal on the porous substrate, thereby catalyzing the porous substrate; and heat-treating the catalyzed porous substrate.





	U	*1	PT	P	Document ID	Issue Date	Pages	Title	Current OR	Current XRef	Retrieval C	Inventor	S	C				
1	☑	☐	☐	☐	US 20030066756 A1	20030410	12	Plating bath and method for depositing a metal layer on	205/296	205/238; 205/241;		Gabe, David R. et al.	☐	☐	☐	☐	☐	☐
2	☑	☐	☐	☐	US 5976344 A	19991102		Composition for electroplating palladium	205/257	106/1.27; 106/1.28;		Abys, Joseph Anthony et al.	☐	☐	☐	☐	☐	☐
3	☑	☐	☐	☐	US 5948222 A	19990907		Reactivation of deactivated anodes	205/115	204/290.13; 204/290.14;		Chen, Chao-Peng et al.	☐	☐	☐	☐	☐	☐
4	☑	☐	☐	☐	US 5863400 A	19990126		Electrochemical cells	205/778	204/192.17; 204/403.11;		Drummond, Humphrey John Jardine et al.	☐	☐	☐	☐	☐	☐
5	☑	☐	☐	☐	US 4923574 A	19900508		Method for making a record member with a metallic	205/83	204/DIG.6; 205/176;		Cohen, Uri	☐	☐	☐	☐	☐	☐
6	☑	☐	☐	☐	US 4911798 A	19900327		Palladium alloy plating process	205/238	205/242; 205/247;		Abys, Joseph A. et al.	☐	☐	☐	☐	☐	☐
7	☑	☐	☐	☐	US 4536259 A	19850820		Cathode having high durability and low hydrogen	205/238	204/290.05; 204/290.06;		Oda, Yoshio et al.	☐	☐	☐	☐	☐	☐
8	☑	☐	☐	☐	US 4486274 A	19841204		Palladium plating prodedure	205/242	205/255; 205/257;		Abys, Joseph A. et al.	☐	☐	☐	☐	☐	☐
9	☑	☐	☐	☐	US 4427502 A	19840124		Platinum and platinum alloy electroplating baths and	205/242	205/255; 205/257;		Abys, Joseph A.	☐	☐	☐	☐	☐	☐
10	☑	☐	☐	☐	US 4410454 A	19831018		Noble metal and rare earth metal catalyst	502/306	205/143; 205/149;		Faschingbauer, Gerald L.	☐	☐	☐	☐	☐	☐
11	☑	☐	☐	☐	US 4197170 A	19800408		Radiation sources and process	205/43	205/135; 205/170;		Malson, Harold A. et al.	☐	☐	☐	☐	☐	☐
12	☑	☐	☐	☐	US 4189358 A	19800219		Electrodeposition of ruthenium-iridium alloy	205/257	204/290.08; 204/290.12;		Scarpellino, Jr, Anthony J. et al.	☐	☐	☐	☐	☐	☐

EAST Browser - L11: [14] 4 and 10 | US 5976344 A | Tag: S | Doc: 1/14 [SORTED] | Format : KWIC

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2	US 5948222 A	7			☑					USPAT
3	US 5863400 A	8			☑					USPAT
4	US 4923574 A	20			☑					USPAT
5	US 4911798 A	7			☑					USPAT
6	US 4536259 A	10			☑					USPAT
7	US 4486274 A	7			☑					USPAT

US-PAT-NO: 5976344

DOCUMENT-IDENTIFIER: US 5976344 A

TITLE: Composition for electroplating palladium alloys and electroplating process using that composition

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Brief Summary Text - BSTX (20):

In order to provide a palladium plating bath which results in stable palladium alloy deposition over a wide range of current densities, the present invention employs a mixed ligand system comprising at least a first ligand to complex the palladium and a second ligand to complex a selected alloying base metal. The alloying base metal is used to harden the palladium deposit for increased wear resistance in connector applications and also to lower the cost in other applications such as corrosion protection or decorative applications. The second ligand is chosen to bring the plating potential of the selected alloying base metal and the plating potential of palladium closer together than they would be in the presence of the first ligand alone. By way of example, the base metal may be at least one of the following: iron (Fe), cobalt (Co), ruthenium (Ru), rhodium (Rh) and iridium (Ir).

Detailed Description Text - DETX (40):

Changes and modifications in the specifically described embodiments can be carried out. For example, based upon the teaching herein, it would be appreciated that in the various Examples 1-4, other alloying metals could also be used to plate Pd alloys including but not limited to Fe, Ir, Rh and Ru. The plating solution taught herein could also be used in plating applications and processes having low current efficiencies (such as strike baths), low metal concentrations as well as low pH values.

Current US Original Classification - CCOR (1):

205/257

United States Patent [19]

Abys et al.

[11] **Patent Number: 5,976,344**

[45] **Date of Patent: Nov. 2, 1999**

[54] **COMPOSITION FOR ELECTROPLATING PALLADIUM ALLOYS AND ELECTROPLATING PROCESS USING THAT COMPOSITION**

[75] Inventors: **Joseph Anthony Abys**, Warren, N.J.; **Irina Boguslavsky**, Naperville, Ill.; **Heinrich K. Straschil**, Summit, N.J.

[73] Assignee: **Lucent Technologies Inc.**, Murray Hill, N.J.

[21] Appl. No.: **08/974,120**

[22] Filed: **Nov. 19, 1997**

Related U.S. Application Data

[63] Continuation of application No. 08/544,347, May 10, 1996, abandoned.

[51] **Int. Cl.**[6] **C25D 3/50**

[52] **U.S. Cl.** 205/257; 205/265; 106/1.27; 106/1.28

[58] **Field of Search** 205/257, 259, 205/265; 106/1.28, 1.27

[56] **References Cited**

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S.N. Vinogradov, et al., Electrolytic Deposition of a Palladium–Cobalt Alloy translated from Zaschita Mettalov, vol. 4, No. 5. pp. 543–547, Sep.–Oct., 1968.

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S.N. Vinogradov, et al, The Electrodeposition of Palladium–Cobalt Alloy from a Complex Electrolyte with Mixed Ligands, translated from Zaschita Metallov, vol. 7, No. 5, pp. 612–613 Sep.–Oct., 1971.

A.I. Zayats, et al., Study of Electrodeposition and Certain Physical Properties of Disperse Palladium–Cobalt Alloys, Translated from Zhurnal Priknadnoi Khimii vol. 45, No. 9, pp. 1948–1953, Sep., 1972.

S.N. Vinogradov, et al., Deposition of Palladium–Cobalt Alloy From an Ammonia Electrolyte, Translated from Zashchita Metallov, vol. 14, No. 3, pp. 362–365, May–Jun., 1978.

E.V. Chumak, et al., Use of Chronopotentiometric Results in Palladium–Cobalt Alloy Electrodeposition Technology, Translated from Elektrokhimiya, vol. 25, No. 12, pp. 1668–1670, Dec., 1989.

Primary Examiner—Kishor Mayekar

Attorney, Agent, or Firm—Gibbons, Del Deo, Dolan, Griffinger & Vecchione

[57] **ABSTRACT**

An aqueous electroplating bath for the electrodeposition of palladium alloys in a mixed ligand system. A first ligand operates to form a complex of palladium and a second ligand functions to form a complex of another metal which brings the plating potentials of the two metals closer together. Palladium and the alloying metal thus exist as complexes with different structures.

8 Claims, No Drawings

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1	US 5976344 A	5							☑				USPAT
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6	US 4536259 A	10						☑					USPAT
7	US 4486274 A	7						☑					USPAT

US-PAT-NO: 4911798

DOCUMENT-IDENTIFIER: US 4911798 A

TITLE: Palladium alloy plating process

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Detailed Description Text - DETX (8):
Most preferred is the compound tris-(hydroxymethyl) aminomethane both because the electroplating potential for the palladium complex is well removed from the hydrogen evolution potential and the electroplating potential for alloying metals (e.g. nickel and cobalt) is close to the electroplating potential for the palladium complex. Typical alloying metals are silver, copper, nickel, cobalt, gold, chromium, manganese, ruthenium, rhodium, platinum and iridium. Particularly useful are copper, nickel, cobalt and silver. Preferred are alloys comprising at least 10 mole percent palladium, remainder copper, nickel, cobalt and/or silver. Other useful alloys are 40, 60 or 80 mole percent palladium, remainder silver, nickel, cobalt and/or silver. Often, the plated palladium or palladium alloy is at least partially covered with a thin (e.g. between 0.01 and 0.5 micrometer thick) layer of gold to improve corrosion resistance and wear resistance.

Detailed Description Text - DETX (26):
Part of the palladium in the electroplating solution is replaced by the following metals: silver, copper, nickel, cobalt, gold, chromium, manganese, ruthenium, rhodium, platinum and iridium. Mole percent of palladium replaced by these metals were 10, 20, 30, 40, and 90. Electroplating was carried out at 65.degree. C., 55.degree. C. and room temperature.

Claims Text - CLTX (3):
3. The process of claim 1 in which the metallic substance comprises, in addition to palladium, at least one metal selected from the group consisting of silver, copper, nickel, cobalt, gold, chromium, manganese, ruthenium, rhodium, platinum and iridium.

Current US Cross Reference Classification - CCXR (3):
205/257

United States Patent [19]
Abys et al.

[11] Patent Number: 4,911,798
[45] Date of Patent: Mar. 27, 1990

[54] **PALLADIUM ALLOY PLATING PROCESS**

[75] Inventors: Joseph A. Abys, Warren; Virginia T. Eckert, Summit; Catherine Wolowodiuk, Chatham Township, Morris County, all of N.J.

[73] Assignee: AT&T Bell Laboratories, Murray Hill, N.J.

[21] Appl. No.: 288,537

[22] Filed: Dec. 20, 1988

[51] Int. Cl.[4] C25D 3/50; C25D 3/56

[52] U.S. Cl. 204/44; 204/43.1; 204/44.3; 204/44.6; 204/47

[58] Field of Search 204/47, 44.6, 44, 44.3, 204/43.1

[56] References Cited

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4,066,517	1/1978	Stevens et al.	204/44.6
4,278,514	7/1981	Morrissey	204/47
4,339,311	7/1982	Bronik	204/47
4,454,010	6/1984	Trop	204/47
4,486,274	12/1984	Abys et al.	204/44
4,778,574	10/1988	Mathe et al.	204/47

FOREIGN PATENT DOCUMENTS

2939920	9/1981	Fed. Rep. of Germany	
263354	2/1970	U.S.S.R.	204/47

OTHER PUBLICATIONS

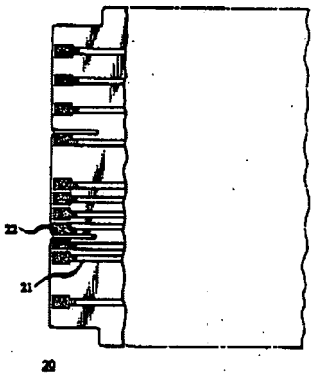
Chem. Abstracts, vol. 72, p. 538, 38158g, (1970).

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Walter G. Nilsen

[57] **ABSTRACT**

A process is described for electroplating palladium and palladium alloys. The process involves the use of an alkyl hydroxyamine as complexing agent and is particularly good for palladium alloys such as palladium-nickel and palladium-cobalt.

11 Claims, 2 Drawing Sheets



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4	US 4923574 A	20									USPAT
5	US 4911798 A	7									USPAT
6	US 4536259 A	10									USPAT
7	US 4486274 A	7									USPAT

US-PAT-NO: 4486274

DOCUMENT-IDENTIFIER: US 4486274 A

TITLE: Palladium plating prodedure

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Detailed Description Text - DETX (5):
Alloy plating may also be carried out using the polyamine complexing agent. Typical elements alloyed with palladium are silver, copper, nickel, cobalt, iron, gold, chromium, manganese, ruthenium, rhodium, platinum and iridium. Particularly useful are copper, nickel and silver. Preferred are alloys comprising at least 10 mole percent palladium, remainder copper, silver and/or nickel. Other useful alloys are 60 mole percent palladium, remainder silver, copper and/or nickel, 40 mole percent palladium, remainder silver, copper and/or nickel, etc. The palladium-silver alloys are particularly useful, especially for electrical contact surfaces.

Current US Cross Reference Classification - CCXR (2):
205/257

United States Patent [19]

Abys et al.

[11] Patent Number: 4,486,274

[45] Date of Patent: Dec. 4, 1984

[54] PALLADIUM PLATING PRODEDURE

[75] Inventors: Joseph A. Abys, Bridgewater; Harvey S. Trop, Morris Plains, both of N.J.

[73] Assignee: AT&T Bell Laboratories, Murray Hill, N.J.

[21] Appl. No.: 477,588

[22] Filed: Mar. 21, 1983

Related U.S. Application Data

[63] Continuation of Ser. No. 239,151, Feb. 27, 1981, abandoned.

[51] Int. Cl.³ C25D 3/52; C25D 3/56; C25D 3/58; C25D 3/64

[52] U.S. Cl. 204/44; 204/43.1; 204/44.6; 204/47

[58] Field of Search ..... 204/47, 43 R, 43 N, 204/43 T, 44, 109, 123

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2506467	8/1976	Fed. Rep. of Germany	204/43 N

Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Walter G. Nilsen

[57] ABSTRACT

A palladium electroplating procedure is disclosed which permits rapid and efficient plating and yields ductile, adherent palladium films. The electroplating bath comprises a unique palladium complex. The procedure is also useful for electroplating a variety of palladium alloys. In addition, the bath is highly stable and does not adversely affect the base material being plated.

24 Claims, 1 Drawing Figure

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9	US 4410454 A	6				☑				USPAT
10	US 4197170 A	9				☑				USPAT
11	US 4189358 A	10				☑				USPAT

US-PAT-NO: 4189358

DOCUMENT-IDENTIFIER: US 4189358 A

TITLE: Electrodeposition of ruthenium-iridium alloy

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Brief Summary Text - BSTX (4):
Several baths have been developed for electroplating ruthenium and for electroplating iridium. Examples of ruthenium electroplating baths can be found in U.S. Pat. Nos. 2,057,638, 2,600,175, 3,123,544, 3,576,724, 3,630,856, 3,793,162 and 4,082,625. Examples of iridium plating baths can be found in U.S. Pat. Nos. 1,077,920 3,554,881, 3,639,219, in Lowenheim's MODERN ELECTROPLATING, 3rd Ed., pp. 354-355 (1974), and in an article by G. A. Conn entitled, "Iridium Plating" in PLATING PROCEEDINGS, pp. 1258-1261, (1965). In general, ruthenium is considered more difficult to plate than such metals as platinum and palladium, and iridium is considered more difficult to plate than ruthenium. Baths for electrodeposition of certain alloys of ruthenium have also been disclosed, e.g., for Ru-Rh, Ru-Pt, and Ru-Pd in U.S. Pat. No. 3,692,641 and for Rh-Ru in U.S. Pat. No. 3,892,638. None of the patents noted above discloses a bath for co-depositing ruthenium and iridium.

Detailed Description Text - DETX (2):
FIGS. 1 and 2 are photomicrographs at 500X magnification which show the quality of a Ru-4-6Ir alloy deposit from a bath of the present invention on two different surfaces. In both samples the substrate is copper polished metallographically to a 1 .mu.m diamond finish, but in FIG. 1 plating is directly on the copper and in FIG. 2 plating is on copper covered with 0.15 mg/cm.sup.2 of palladium. FIG. 1, with plating directly on copper, shows cracks at a Ru-Ir loading of 1 mg/cm.sup.2. FIG. 2, with plating on the palladium coated copper, shows no cracks at a Ru-Ir loading of 1.9 mg/cm.sup.2.

Detailed Description Text - DETX (28):
Advantageously, particularly for electrowinning applications the valve metal can be coated with a barrier layer, e.g. comprising platinum group metals, gold and nitrides, carbides and silicides of one of the components of the substrate. As shown in FIGS. 1 and 2 a palladium coating, e.g. on a polished copper surface, improved the quality of the deposit. Similar findings have been made with gold and iridium coatings on copper.

Detailed Description Text - DETX (29):
As used herein, the term "alloy" as applied to a ruthenium-iridium deposit, means that the film contains a mixture of very fine particles of ruthenium and iridium which has a metallic appearance. The particles may be mixed crystals or in solid solution, the microscopic character of the deposited films being different to determine because films are very thin. By "valve" metals is meant those metals form oxide films under anodic conditions, as do, for example, titanium, tantalum, niobium, tungsten, zirconium, aluminum, hafnium and alloys thereof with each other and with other metals. The platinum group metals are platinum, palladium, rhodium, ruthenium, osmium and iridium. The terms electroplated and electrodeposited are used interchangeably. The abbreviations

United States Patent [19]

Scarpellino, Jr et al.

[11] **4,189,358**

[45] **Feb. 19, 1980**

[54] **ELECTRODEPOSITION OF RUTHENIUM-IRIDIUM ALLOY**

[75] Inventors: **Anthony J. Scarpellino, Jr, Tuxedo, N.Y.; William G. Borner, Ringwood, N.J.**

[73] Assignee: **The International Nickel Company, Inc., New York, N.Y.**

[21] Appl. No.: **924,632**

[22] Filed: **Jul. 14, 1978**

[51] Int. Cl.[2] **C25D 3/50; C25B 11/08; C25B 11/10; C25C 1/00**

[52] U.S. Cl. ..... **204/43 N; 204/105 R; 204/105 M; 204/106; 204/108; 204/107; 204/109; 204/110; 204/111; 204/112; 204/113; 204/114; 204/115; 204/116; 204/117; 204/123; 204/290R; 204/290 F; 204/293**

[58] Field of Search ..... **204/290 R, 290 F, 293, 204/43 N, 48-49, 112-113, 105 R, 106-108, 109-111, 114-117, 105 M, 123**

[56] **References Cited**

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3,846,273	11/1974	Bianchi et al.	204/290 F

Primary Examiner—R. L. Andrews
Attorney, Agent, or Firm—Ewan C. MacQueen; Miriam W. Leff

[57] **ABSTRACT**

Ruthenium-iridium electrodeposits are prepared from aqueous acid solution containing ruthenium, iridium, a fluoborate salt, fluoboric acid, and optionally sulfamic acid. The baths are especially useful for preparing insoluble anodes.

38 Claims, 2 Drawing Figures

EAST Browser - L11: (14) 4 and 10 | US 3933602 A | Tag: S | Doc: 13/14 (SORTED) | Format: KWIC

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	Document ID	Pages	1		3			U	S	C	P	Kind Codes	Sou
7	US 4486274 A	7							☑				USPAT
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11	US 4189358 A	10							☑				USPAT
12	US 4160704 A	6							☑				USPAT
13	US 3933602 A	7							☑				USPAT

US-PAT-NO: 3933602

DOCUMENT-IDENTIFIER: US 3933602 A
See image for Certificate of Correction

TITLE: Palladium electroplating bath, process, and preparation

---------- KWIC ---------

Detailed Description Text - DETX (6):
The other metals which can provide deposits of palladium alloys by the electrolysis of the present bath are much varied. Practically, most common or base metals and precious metals are suitable. As such, the following can be mentioned: Cd, Cr, Co, Cu, Ga, Au, In, Fe, Pb, Mo, Ni, Ag, Sn, V, Zn. However, in special cases, it is also possible to incorporate in the present bath metals such as As, Sb and Bi or noble metals of the platinum group such as Pt, Rh, Ru, Ir and Os. These metals can be present in the bath in the form of their water soluble salts or complexes generally used in the electroplating art with the exception, naturally of nitrates and nitrites. Among the derivatives of said metals the following will be preferably used: salts, e.g., halides, sulfates, sulfites, phosphates, pyrophosphates, salts with organic acids, e.g., acetates, formates, or chelates with conventional chelatants, e.g., ethylene diamine (en), ethylenediamine tetraacetic acid (EDTA) and ethylenediamine tetramethanephosphonic acid (EDTP). It is clear that the kind of each of said different metal compounds must be chosen as a function of their mutual compatibility and solubility in the bath.

Current US Original Classification - CCOR (1):
205/257

United States Patent [19]

Henzi et al.

[11] 3,933,602

[45] Jan. 20, 1976

[54] PALLADIUM ELECTROPLATING BATH, PROCESS, AND PREPARATION

[75] Inventors: René Henzi; André Meyer, both of Geneva, Switzerland; Pierre Lalanne, Gex, France

[73] Assignee: Oxy Metal Industries Corporation, Detroit, Mich.

[22] Filed: Apr. 19, 1974

[21] Appl. No.: 462,484

[30] Foreign Application Priority Data

Apr. 27, 1973 Switzerland 6142/73

[52] U.S. Cl. ..... 204/44; 204/43 N; 204/47; 423/22; 423/351; 423/512

[51] Int. Cl.²..... C25D 3/50; C25D 3/52; C25D 3/56

[58] Field of Search ..... 204/47, 43 N, 44

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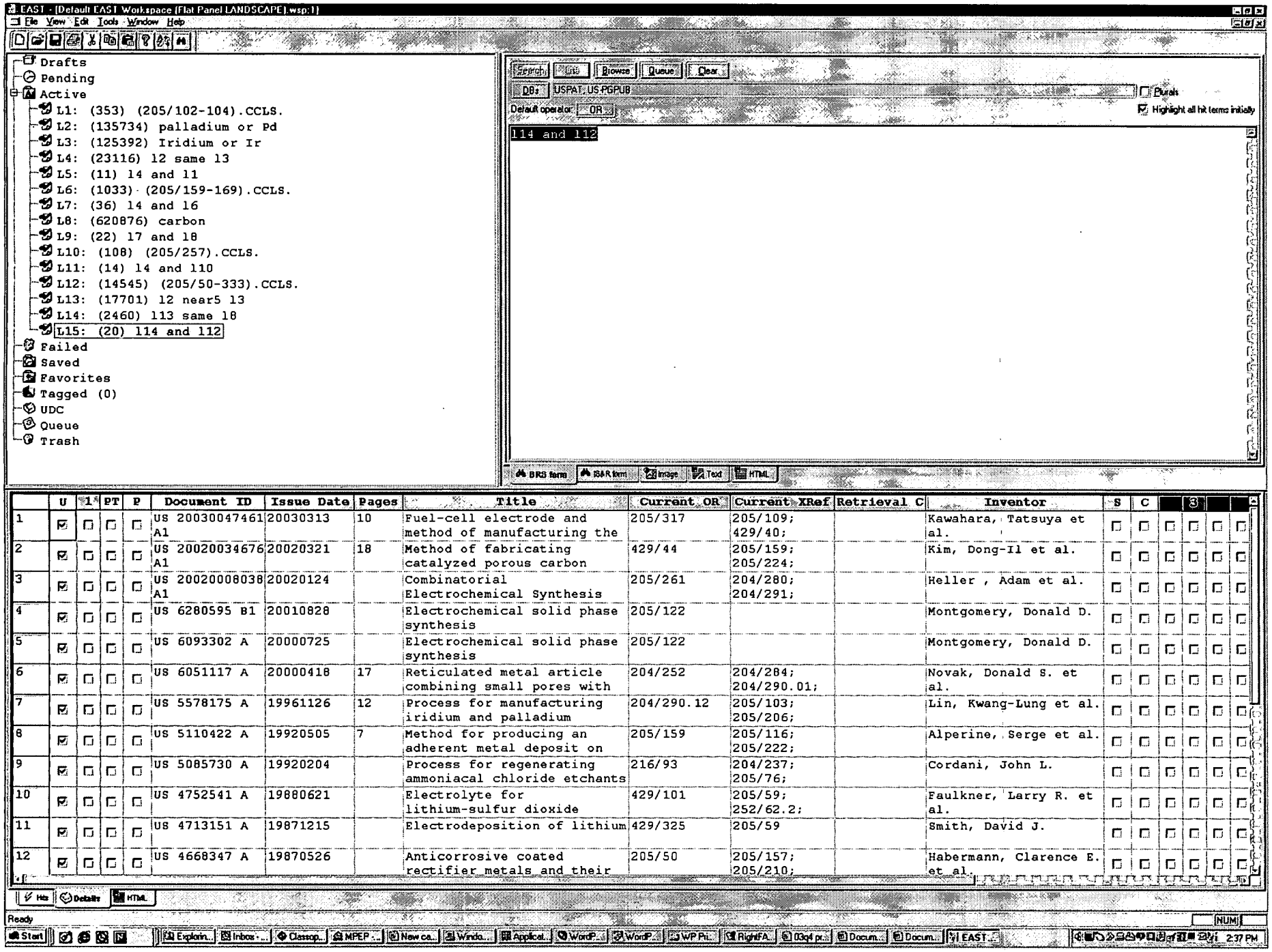
Primary Examiner—G. L. Kaplan
Attorney, Agent, or Firm—Arthur E. Kluegel; B. F. Claeboe; Richard P. Mueller

[57] ABSTRACT

Disclosed is an aqueous plating bath suitable for obtaining electrodeposits of palladium and its alloys. The bath is substantially free of cyanide, nitrate and nitrite, and comprises sulfite ion, palladium in the form of a tetra-coordinated complex with palladium in the +2 oxidation state, an atomic ratio of halide to palladium not in excess of 10, and exhibits a pH of from 7 to 12.

7 Claims, No Drawings



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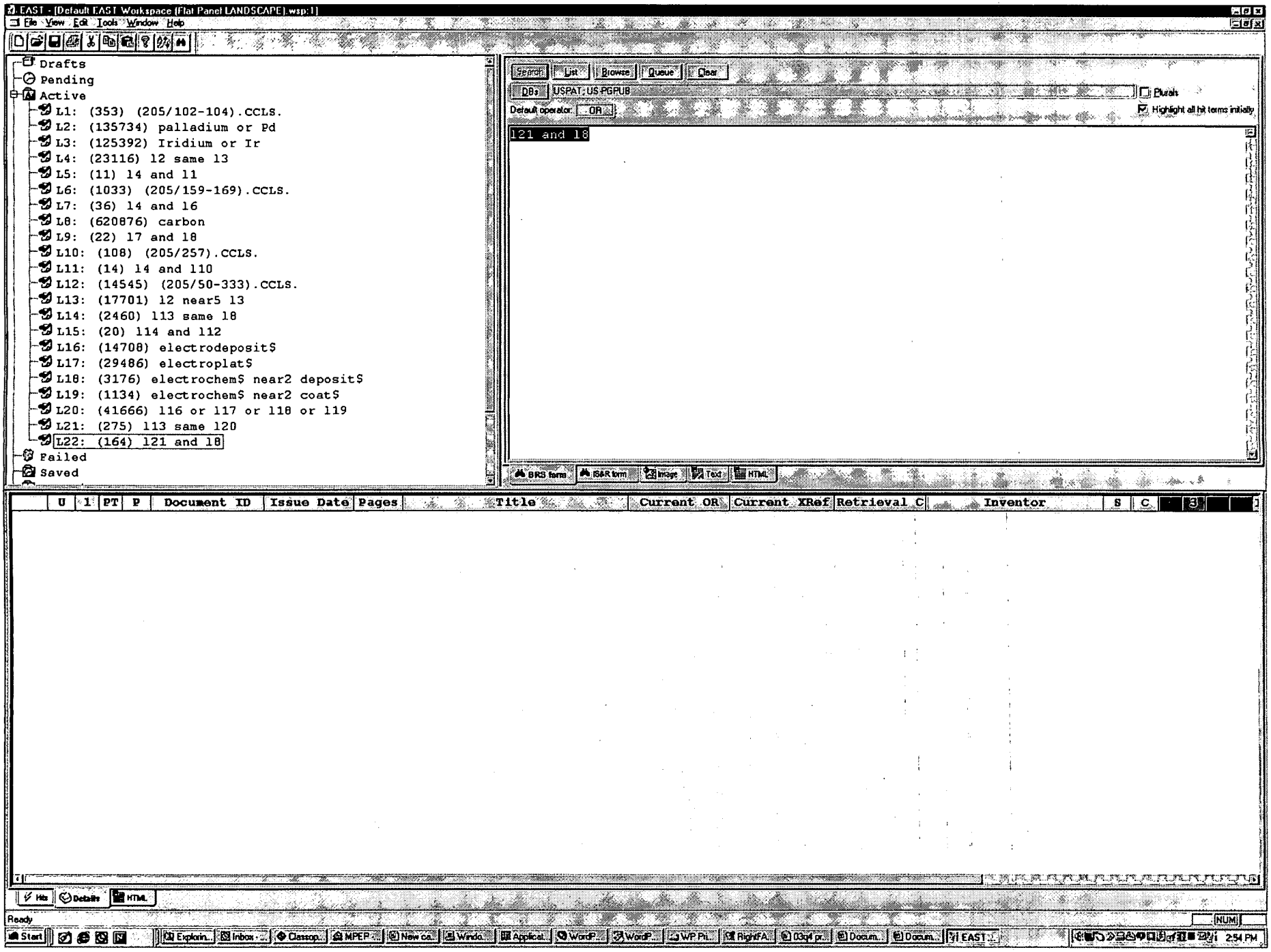
1	☑	☐	☐	☐	US 20030047461 A1	20030313	10	Fuel-cell electrode and method of manufacturing the	205/317	205/109; 429/40;		Kawahara, Tatsuya et al.	☐	☐	☐	☐	☐	☐
2	☑	☐	☐	☐	US 20020034676 A1	20020321	18	Method of fabricating catalyzed porous carbon	429/44	205/159; 205/224;		Kim, Dong-Il et al.	☐	☐	☐	☐	☐	☐
3	☑	☐	☐	☐	US 20020008038 A1	20020124		Combinatorial Electrochemical Synthesis	205/261	204/280; 204/291;		Heller , Adam et al.	☐	☐	☐	☐	☐	☐
4	☑	☐	☐	☐	US 6280595 B1	20010828		Electrochemical solid phase synthesis	205/122			Montgomery, Donald D.	☐	☐	☐	☐	☐	☐
5	☑	☐	☐	☐	US 6093302 A	20000725		Electrochemical solid phase synthesis	205/122			Montgomery, Donald D.	☐	☐	☐	☐	☐	☐
6	☑	☐	☐	☐	US 6051117 A	20000418	17	Reticulated metal article combining small pores with	204/252	204/284; 204/290.01;		Novak, Donald S. et al.	☐	☐	☐	☐	☐	☐
7	☑	☐	☐	☐	US 5578175 A	19961126	12	Process for manufacturing iridium and palladium	204/290.12	205/103; 205/206;		Lin, Kwang-Lung et al.	☐	☐	☐	☐	☐	☐
8	☑	☐	☐	☐	US 5110422 A	19920505	7	Method for producing an adherent metal deposit on	205/159	205/116; 205/222;		Alperine, Serge et al.	☐	☐	☐	☐	☐	☐
9	☑	☐	☐	☐	US 5085730 A	19920204		Process for regenerating ammoniacal chloride etchants	216/93	204/237; 205/76;		Cordani, John L.	☐	☐	☐	☐	☐	☐
10	☑	☐	☐	☐	US 4752541 A	19880621		Electrolyte for lithium-sulfur dioxide	429/101	205/59; 252/62.2;		Faulkner, Larry R. et al.	☐	☐	☐	☐	☐	☐
11	☑	☐	☐	☐	US 4713151 A	19871215		Electrodeposition of lithium	429/325	205/59		Smith, David J.	☐	☐	☐	☐	☐	☐
12	☑	☐	☐	☐	US 4668347 A	19870526		Anticorrosive coated rectifier metals and their	205/50	205/157; 205/210;		Habermann, Clarence E. et al.	☐	☐	☐	☐	☐	☐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L8: (620876) carbon
L9: (22) l7 and l8
L10: (108) (205/257).CCLS.
L11: (14) l4 and l10
L12: (14545) (205/50-333).CCLS.
L13: (17701) l2 near5 l3
L14: (2460) l13 same l8
L15: (20) l14 and l12
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L17: (29486) electroplat$
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33	US 6179988 B1	23		USPAT
34	US 6163947 A	15		USPAT
35	US 6161782 A	14		USPAT
36	US 6153352 A	36		USPAT
37	US 6119485 A	16		USPAT
38	US 6117286 A	11		USPAT

Brief Summary Text - BSTX (17):

(1) The carbon used as an electrode material readily deteriorates at high temperatures in the presence of both sodium hydroxide and oxygen to considerably impair electrode performance.

Brief Summary Text - BSTX (23):

(7) If air is utilized as an oxygen-containing gas, the gas-diffusing ability of the electrode is reduced. This is because carbon dioxide contained in the air reacts with sodium hydroxide to deposit sodium carbonate on the walls of the pores of the gas diffusion electrode.

Detailed Description Text - DETX (11):

The oxygen gas diffusion cathode for use in the present invention may have the characteristics of conventional oxygen gas diffusion cathodes. For example, a gauze, sintered powder, sintered metal fiber, foamed object, etc., made of a corrosion-resistant material such as, e.g., titanium, niobium, tantalum, stainless steel, nickel, zirconium, carbon, or silver can be used as an electrode substrate, optionally after having been cleaned in a pretreatment. It is preferred to impart moderate porosity and electroconductivity to this electrode substrate so as to smoothly conduct the feeding and removal of electric current and also of the gas and liquid.

Detailed Description Text - DETX (12):

A catalyst layer is desirably formed on the surface of the electrode substrate. The catalyst can be made of a metal such as, e.g., platinum, palladium, ruthenium, iridium, copper, silver, cobalt, or lead or an oxide of any of these metals. A layer of the catalyst can be formed by mixing a catalyst material powder with a binder, e.g., a fluororesin, and a solvent, e.g., naphtha, depositing the resultant paste on the substrate, and solidifying the deposit, or by applying a solution of a salt of a catalyst metal on the substrate surface and burning the coating, or by subjecting the substrate to electroplating in the salt solution or to electroless plating in the salt solution in the presence of a reducing agent.

Detailed Description Text - DETX (15):

The hydrophilic material interposed between the ion-exchange membrane and the gas diffusion cathode in the present invention is preferably a porous structure comprising a corrosion-resistant metal or resin. This hydrophilic material need not have electroconductivity because it does not contribute to electron movement. Examples of the hydrophilic material include carbon, ceramics such as zirconium oxide and silicon carbide, hydrophilized resins such as PTFE and EEP, metals such as nickel, stainless steel, and silver, and alloys of such metals. The hydrophilic material is preferably in the form of a sheet having a thickness of from 0.01 to 10 mm. Because the hydrophilic material is interposed between the membrane and the cathode, it is desirably an elastic material which, when pressure unevenness is present, deforms to absorb the pressure. Furthermore, the hydrophilic material preferably is made of such a material, and has a structure which can hold a catholyte. Examples of such structures include nets, woven fabrics, nonwoven fabrics and foamed objects. Especially preferred is a sintered plate obtained by mixing a powdery starting material with a pore-forming agent and any of various binders, molding the mixture into a sheet, removing the pore-forming agent with a solvent, and then sintering the sheet, or a structure composed of such sintered plates superposed on each other. An appropriate range of the pore diameter of this hydrophilic

United States Patent [19]

Shimamune et al.

[11] **Patent Number: 6,117,286**

[45] **Date of Patent: Sep. 12, 2000**

[54] **ELECTROLYTIC CELL EMPLOYING GAS DIFFUSION ELECTRODE**

[75] Inventors: **Takayuki Shimamune**, Tokyo; **Koichi Aoki**, Fukui; **Masashi Tanaka**, Kanagawa; **Katsumi Hamaguchi**, Kanagawa; **Yoshinori Nishiki**, Kanagawa, all of Japan

[73] Assignee: **Permelec Electrode Ltd.**, Kanagawa, Japan

[21] Appl. No.: **09/173,686**

[22] Filed: **Oct. 16, 1998**

[30] **Foreign Application Priority Data**

Oct. 16, 1997 [JP] Japan 9-299563

[51] **Int. Cl.**[7] **C25B 9/10**

[52] **U.S. Cl.** **204/252**; 204/263; 204/282; 204/283

[58] **Field of Search** 204/283, 252, 204/263, 282

[56] **References Cited**

U.S. PATENT DOCUMENTS

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5,039,389	8/1991	McMichael	204/282
5,766,429	6/1998	Shimamune et al.	204/283

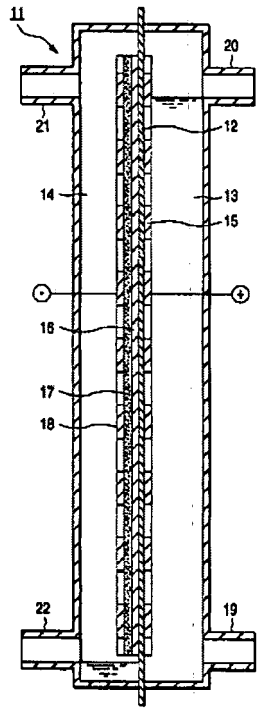
Primary Examiner—Bruce F. Bell

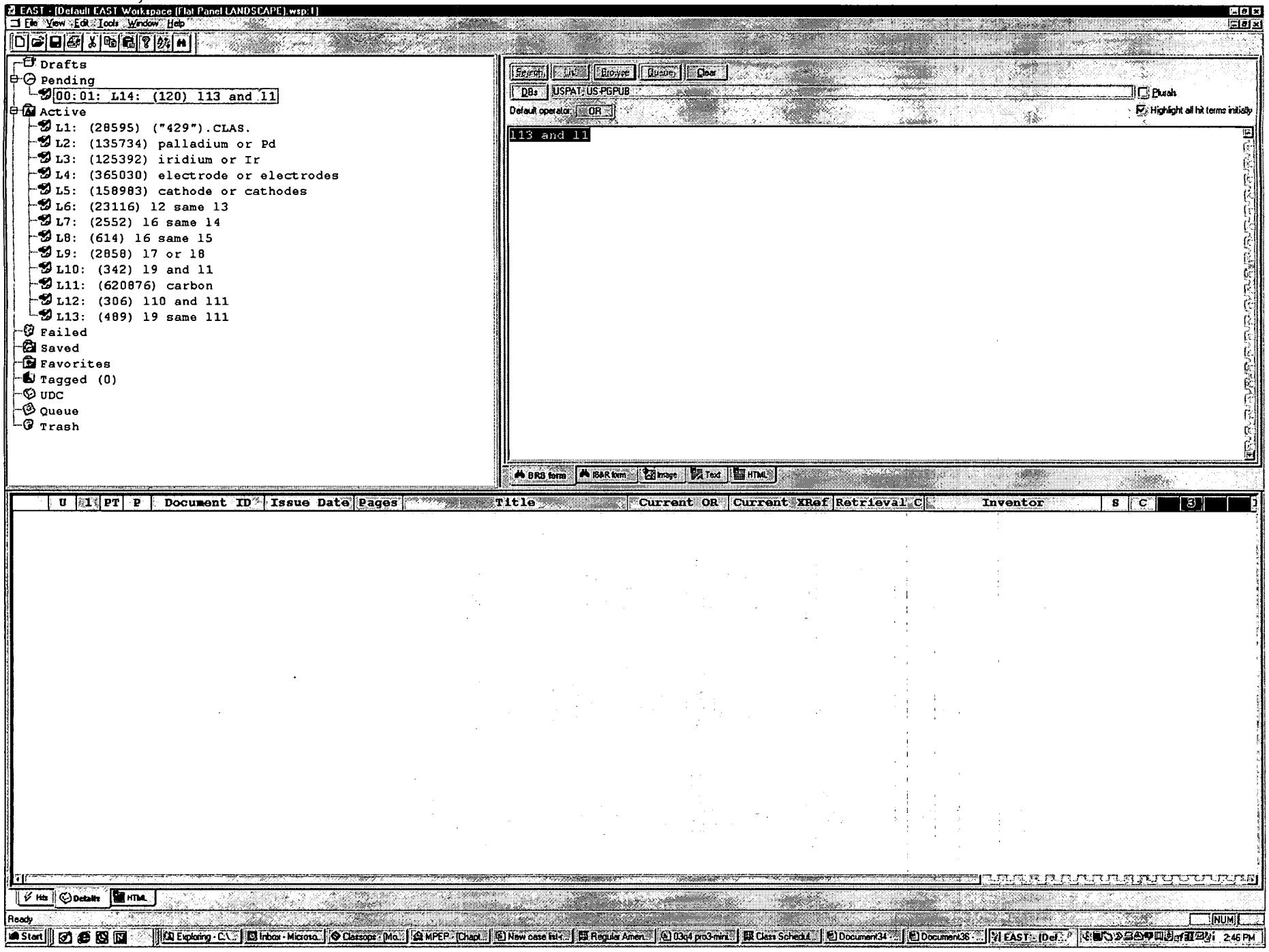
Attorney, Agent, or Firm—Sughrue, Mion, Zinn, Macpeak & Seas, PLLC

[57] **ABSTRACT**

A zero-gap type electrolytic cell 11 characterized as having a hydrophilic liquid-permeable material 16 interposed between an ion-exchange membrane 12 and a gas diffusion cathode 17. The reaction product passes through the liquid-permeable material and disperses toward edges of the liquid-permeable material before being withdrawn. Hence, the withdrawal direction for the target reaction product is not opposite the feed direction for the reactant gas.

28 Claims, 3 Drawing Sheets

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L5: (158983) cathode or cathodes
L6: (23116) l2 same l3
L7: (2552) l6 same l4
L8: (614) l6 same l5
L9: (2858) l7 or l8
L10: (342) l9 and l1
L11: (620876) carbon
L12: (306) l10 and l11
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13	US 6332900 B1	5							☑				USPAT
14	US 6326098 B1	11							☑				USPAT
15	US 6284402 B1	12							☑				USPAT
16	US 6171721 B1	10							☑				USPAT

US-PAT-NO: 6171721

DOCUMENT-IDENTIFIER: US 6171721 B1

TITLE: Sputter-deposited fuel cell membranes and electrodes

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Detailed Description Text - DETX (16):

Targets 4 may be sputter-deposited onto an anode carrier, a cathode carrier, carbon paper, or other suitable material. The resulting sputter-coated carrier or paper materials are used to fabricate MEAs. Carrier materials useful for fabricating anodes and cathodes and methods for preparing the carrier materials, including methods to alter the wettability of the carriers, are known. To use the methods described herein to prepare an electrode, a suitable carrier such as carbon paper is suitably secured to the substrate holder 8. Once secured, the suitable carrier is sputter-coated using any of the target 4 materials disclosed herein by following the methods described for sputter-coating electrolyte membranes. For example, if an anode is being constructed, the target 4 material should contain catalysts appropriate for the anode such as a platinum-ruthenium alloy. Alternatively, if a cathode surface is being produced, the target 4 material should contain catalysts appropriate for the cathode such as platinum. Other useful target materials include Ni, Ti, Zr, Sn, SnO.sub.2, Ru, Pt, Os, Ir, W, WO.sub.3, Re, Pd, Mo, Nb, RuO.sub.2, alloys thereof, and other similar materials.

Current US Class - CLAS (2):

429

(12) **United States Patent**
Narayanan et al.

(10) **Patent No.: US 6,171,721 B1**
(45) **Date of Patent: Jan. 9, 2001**

(54) **SPUTTER-DEPOSITED FUEL CELL MEMBRANES AND ELECTRODES**

(75) Inventors: **Sekharipuram R. Narayanan**, Altadena; **Barbara Jeffries-Nakamura**, St. Marino; **William Chun**, Los Angeles; **Ron P. Ruiz**, Alhambra; **Thomas I. Valdez**, Covina, all of CA (US)

(73) Assignee: **California Institute of Technology**, Pasadena, CA (US)

(*) Notice: Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days.

(21) Appl. No.: 09/172,104

(22) Filed: Sep. 22, 1998

Related U.S. Application Data

(60) Provisional application No. 60/059,472, filed on Sep. 22, 1997.

(51) Int. Cl.[7] H01M 11/00

(52) U.S. Cl. ..... 429/41; 429/42; 429/44; 429/40; 204/290 R; 204/283; 204/192.14; 204/296

(58) Field of Search ..... 204/290 R, 192.14, 204/283, 294, 296; 429/40, 41, 42, 44

(56) **References Cited**

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Primary Examiner—Bruce F. Bell
(74) *Attorney, Agent, or Firm*—Fish & Richardson P.C.

(57) **ABSTRACT**

A method for preparing a membrane for use in a fuel cell membrane electrode assembly includes the steps of providing an electrolyte membrane, and sputter-depositing a catalyst onto the electrolyte membrane. The sputter-deposited catalyst may be applied to multiple sides of the electrolyte membrane. A method for forming an electrode for use in a fuel cell membrane electrode assembly includes the steps of obtaining a catalyst, obtaining a backing, and sputter-depositing the catalyst onto the backing. The membranes and electrodes are useful for assembling fuel cells that include an anode electrode, a cathode electrode, a fuel supply, and an electrolyte membrane, wherein the electrolyte membrane includes a sputter-deposited catalyst, and the sputter-deposited catalyst is effective for sustaining a voltage across a membrane electrode assembly in the fuel cell.

61 Claims, 3 Drawing Sheets

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15	US 6284402 B1	12				☑				USPAT
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18	US 6143443 A	90				☑				USPAT
19	US 6131851 A	6				☑				USPAT
20	US 6127061 A	16				☑				USPAT

US-PAT-NO: 6127061

DOCUMENT-IDENTIFIER: US 6127061 A

TITLE: Catalytic air cathode for air-metal batteries

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Brief Summary Text - BSTX (14):

Thin porous carbon paper based electrodes, such as disclosed in U.S. Pat. No. 3,912,538, solves the bulk problem and has a shortened diffusion path. Unfortunately, thin porous carbon paper substrates are very fragile, and they are subject to excessive flooding with electrolyte which interferes with the access of the gas to the electro catalytic sites of the electrodes. To control the flooding, the carbon papers are often rendered hydrophobic by means of, for example, a Teflon coating which increases their electrical resistivity. In addition, because they are structurally weak, they tend to break in handling, as well as when they operate under moderate gas pressures. Finally, the wet-proofed carbon papers have to be dense to provide a minimum of structural integrity. This characteristic confines a catalytic layer to a surface coating bonded merely to one face of the paper substrate, and being paper, they are inherently nonuniform with respect to porosity. Another thin electrolytic gas diffusion electrode comprises a substantially uniform, open pore carbon or graphite substrate, having a thickness in the range to about 5 to 40 mils, and preferably about 10 to about 35 mils and includes a mixture of Teflon or similar wet-proofing particles and catalytic carbon particles imbedded and added within the cloth pores. This type electrode has improved electrochemical performances as well as improve structural strength and is suitable for use in free-flowing electrolytic electrochemical cells. The catalytic carbon particles are either metal-free catalytic carbon particles or finely divided high surface area carbons carrying suitable known noble metal catalytic particles, including platinum, palladium, radium, iridium, ruthenium, and silver, depending on the environment (e.g., acid or alkaline, air or hydrogen, and on operating conditions: temperature, current density and intended length of service).

Current US Class - CLAS (1):

429

United States Patent [19]

Shun et al.

[11] **Patent Number: 6,127,061**

[45] **Date of Patent: Oct. 3, 2000**

[54] **CATALYTIC AIR CATHODE FOR AIR-METAL BATTERIES**

[75] Inventors: You-Keung Shun, South Shanghai; Chou-Lui Lou, Shenzhen, both of China

[73] Assignee: High-Density Energy, Inc., Azusa, Calif.

[21] Appl. No.: 09/238,008

[22] Filed: Jan. 26, 1999

[51] Int. Cl.[7] H01M 4/86

[52] U.S. Cl. 429/40; 429/42; 429/44; 429/27; 429/59; 429/133; 429/162; 429/163; 429/164; 429/165

[58] Field of Search ..... 429/42, 40, 44, 429/27, 12, 59, 133, 162, 163, 164, 165; 204/282, 283, 290 R

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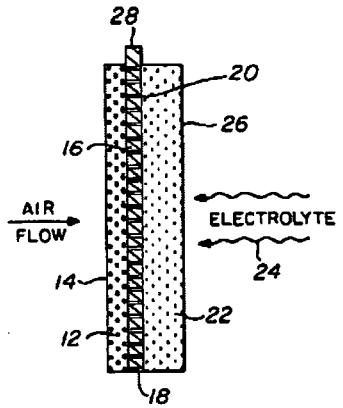
Primary Examiner—Bruce F. Bell

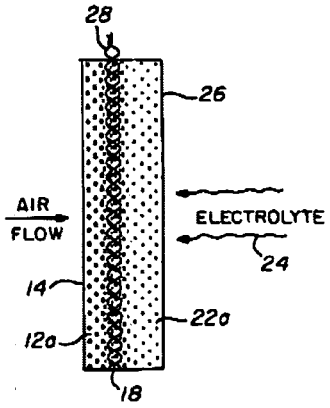
Attorney, Agent, or Firm—Jones, Day, Reavis & Pogue

[57] **ABSTRACT**

An air cathode for use in an electrochemical cell or battery having an air permeable and water impermeable layer, an electrically conductive middle layer and a catalytic layer comprising a mixture of carbon particles, particulate materials, having a high surface area, metal hydroxides, and hydrophobic particles.

59 Claims, 6 Drawing Sheets





EAST Browser - L14: [120] 13 and 1 | US 5716437 A | Tag: S | Doc: 20/120 (SORTED) | Format: KWIC

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	Document ID	Pages	1	2	3			U	S	C	P/N	Kind Codes	Sou
22	US 6045938 A	7							☑				USPAT
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26	US 5783325 A	14							☑				USPAT
27	US 5729427 A	10							☑				USPAT
28	US 5716437 A	13							☑				USPAT

US-PAT-NO: 5716437

DOCUMENT-IDENTIFIER: US 5716437 A

TITLE: Materials for use in electrode manufacture

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Brief Summary Text - BSTX (28):
The term "catalyst" will be well understood by a person skilled in the art by meaning a catalyst that when incorporated into a gas diffusion electrode facilitates an electrochemical reaction, for example the catalyst may be selected from the platinum group metals (ie platinum, palladium, rhodium, ruthenium, iridium and osmium), gold, silver or a base metal or base metal oxide, or an alloy or mixture comprising one or more of these metals, preferably supported on a conductive substrate, such as carbon.

Current US Class - CLAS (4):
429

United States Patent [19]

Denton et al.

[11] **Patent Number: 5,716,437**

[45] **Date of Patent: Feb. 10, 1998**

[54] **MATERIALS FOR USE IN ELECTRODE MANUFACTURE**

[75] Inventors: **Jan Denton**, Reading; **John M Gascoyne**, High Wycombe; **David Thompsett**, Reading, all of Great Britain

[73] Assignee: **Johnson Matthey Public Limited Company**, London, England

[21] Appl. No.: 613,387

[22] Filed: Mar. 7, 1996

[30] Foreign Application Priority Data

Mar. 9, 1995 [GB] United Kingdom 9504713

[51] Int. Cl.[6] C09D 11/00

[52] U.S. Cl. ..... 106/31.92; 252/514; 204/282; 204/283; 204/286; 204/290 R; 204/291; 204/292; 204/295; 429/40; 429/42; 429/44; 429/45

[58] Field of Search ..... 106/20 B, 31.92; 252/514; 204/282, 283, 286, 290 R, 291, 292, 295; 429/40, 42, 44, 45

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Primary Examiner—Bruce F. Bell

Attorney, Agent, or Firm—Cushman Darby & Cushman IP Group Pillsbury Madison & Sutro LLP

[57] **ABSTRACT**

An improved ink material, particularly for use in printing processes and its use in improved manufacturing processes for higher performance electrodes for application in fuel cells and other electrochemical devices is disclosed.

17 Claims, 5 Drawing Sheets

EAST Browser - L12: (14) 10 same 11 | US 5865881 A | Tag: 5 | Doc: 4/14 (SORTED) | Format : KWIC

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	Document ID	Pages	1	2	3			U	S	C	P	Kind Codes	Sou
1	US RE36330 E	12							☑				USPAT
2	US 5997830 A	16							☑				USPAT
3	US 5981161 A	21							☑				USPAT
4	US 5865881 A	9							☑				USPAT
5	US 5518976 A	13						☑					USPAT
6	US 5487268 A	8						☑					USPAT
7	US 5362619 A	14						☑					USPAT

US-PAT-NO: 5865881

DOCUMENT-IDENTIFIER: US 5865881 A

TITLE: Electroless plating bath of iridium

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Brief Summary Text - BSTX (17):
The iridium halide and/or halogenoiridate is H.sub.2 IrCl.sub.6. 6H.sub.2 O, Na.sub.2 IrCl.sub.6, K.sub.2 IrCl.sub.6, K.sub.3 IrCl.sub.6, IrCl.sub.3, IrCl.sub.4.H.sub.2 O, or a mixture thereof.

Detailed Description Text - DETX (29):
H.sub.2 IrCl.sub.6.6H.sub.2 O, Na.sub.2 IrCl.sub.6, K.sub.2 IrCl.sub.6, K.sub.3 IrCl.sub.6, IrCl.sub.3, IrCl.sub.4.H.sub.2 O, etc. are exemplified as iridium halide and/or halogenoiridate. These are used singly or in combination.

United States Patent [19]

Mori et al.

[11] **Patent Number: 5,865,881**

[45] **Date of Patent: Feb. 2, 1999**

[54] **ELECTROLESS PLATING BATH OF IRIDIUM**

[75] Inventors: **Hiroaki Mori, Toyonaka; Shoji Maezawa, Kawasaki; Keisuke Oguro, Ikeda-Shi; Eiichi Torikai, Yao, all of Japan**

[73] Assignees: **Research Institute of Innovative Technology; Agency of Industrial Science and Technology**

[21] Appl. No.: **851,727**

[22] Filed: **May 6, 1997**

Related U.S. Application Data

[63] Continuation of Ser. No. 564,785, Nov. 29, 1995, abandoned.

[30] **Foreign Application Priority Data**

Dec. 1, 1994 [JP] Japan 6-298227

[51] **Int. Cl.**[6] **C23C 18/54**

[52] **U.S. Cl.** **106/1.28; 427/306**

[58] **Field of Search** 106/1.28; 427/436

[56] **References Cited**

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Primary Examiner—Kathryn L. Gorgos
Assistant Examiner—Kishor Mayekar
Attorney, Agent, or Firm—Armstrong, Westerman, Hattori, McLeland & Naughton

[57] **ABSTRACT**

The present invention relates to a plating bath of the hydrazine type for electroless plating on the surface of a plated substance with iridium. The first plating bath is an electroless plating bath of iridium which contains a hydrazine complex of iridium and has pH of 1–7. The second plating bath is an electroless plating bath of iridium which contains hydrazine hydrate and/or hydrazinium salt, and iridium halide and/or halogenoiridate in the molar ratio of 1–1.0 and has pH of lower than 3. The plating bath of this invention is used, for example, for producing of a junction of a cation exchange membrane and iridium, which is used for a water electrolytic cell of the macromolecule solid electrolyte type.

6 Claims, 2 Drawing Sheets